



Ambient Groundwater Quality of the Tiger Wash Basin

A 2014 Baseline Study
By Douglas Towne

Arizona Department of Environmental Quality
Water Quality Division
Surface Water Section, Monitoring Unit
1110 West Washington Street
Phoenix, AZ 85007-2935
Publication Number: OFR-14-07



Ambient Groundwater Quality of the Tiger Wash Basin: A 2014 Baseline Study

By Douglas C. Towne

Arizona Department of Environmental Quality Open File Report 14-07

ADEQ Water Quality Division
Surface Water Section
Monitoring Unit
1110 West Washington St.
Phoenix, Arizona 85007-2935

Thanks:

Field Assistance: Elizabeth Boettcher and Jade Dickens. Special recognition is extended to Clayton Overson for assisting with groundwater data collection on his ranch.

Photo Credits: Douglas Towne

Report Cover: Little Horn windmill, named after a nearby rock outcrop, was one of five wells sampled for the Tiger Wash basin study. The small, remote basin located west of Phoenix in the Lower Sonoran desert is used almost exclusively for livestock grazing and recreation.

ADEQ Ambient Groundwater Quality Open-File Reports (OFR) and Factsheets (FS):

Avra Valley Sub-basin	OFR 14-06, 66 p.	FS 14-11, 5 p.
Harquahala Basin	OFR 14-04, 62 p.	FS 14-09, 5 p.
Tonto Creek Basin	OFR 13-04, 50 p.	FS 13-18, 4 p.
Upper Hassayampa Basin	OFR 13-03, 52 p.	FS 13-11, 3 p.
Aravaipa Canyon Basin	OFR 13-01, 46 p.	FS 13-04, 4 p.
Butler Valley Basin	OFR 12-06, 44 p.	FS 12-10, 5.p.
Cienega Creek Basin	OFR 12-02, 46 p.	FS 12-05, 4.p.
Ranegras Plain Basin	OFR 11-07, 63 p.	FS 12-01, 4.p.
Groundwater Quality in Arizona	OFR 11-04, 26 p.	-
Bill Williams Basin	OFR 11-06, 77 p.	FS 12-01, 4.p.
San Bernardino Valley Basin	OFR 10-03, 43 p.	FS 10-31, 4 p.
Dripping Springs Wash Basin	OFR 10-02, 33 p.	FS 11-02, 4 p.
McMullen Valley Basin	OFR 11-02, 94 p.	FS 11-03, 6 p.
Gila Valley Sub-basin	OFR 09-12, 99 p.	FS 09-28, 8 p.
Agua Fria Basin	OFR 08-02, 60 p.	FS 08-15, 4 p.
Pinal Active Management Area	OFR 08-01, 97 p.	FS 07-27, 7 p.
Hualapai Valley Basin	OFR 07-05, 53 p.	FS 07-10, 4 p.
Big Sandy Basin	OFR 06-09, 66 p.	FS 06-24, 4 p.
Lake Mohave Basin	OFR 05-08, 66 p.	FS 05-21, 4 p.
Meadview Basin	OFR 05-01, 29 p.	FS 05-01, 4 p.
San Simon Sub-Basin	OFR 04-02, 78 p.	FS 04-06, 4 p.
Detrital Valley Basin	OFR 03-03, 65 p.	FS 03-07, 4 p.
San Rafael Basin	OFR 03-01, 42 p.	FS 03-03, 4 p.
Lower San Pedro Basin	OFR 02-01, 74 p.	FS 02-09, 4 p.
Willcox Basin	OFR 01-09, 55 p.	FS 01-13, 4 p.
Sacramento Valley Basin	OFR 01-04, 77 p.	FS 01-10, 4 p.
Upper Santa Cruz Basin (w/ USGS)	OFR 00-06, 55 p.	-
Prescott Active Management Area	OFR 00-01, 77 p.	FS 00-13, 4 p.
Upper San Pedro Basin (w/ USGS)	OFR 99-12, 50 p.	FS 97-08, 2 p.
Douglas Basin	OFR 99-11, 155 p.	FS 00-08, 4 p.
Virgin River Basin	OFR 99-04, 98 p.	FS 01-02, 4 p.
Yuma Basin	OFR 98-07, 121 p.	FS 01-03, 4 p.

These publications are available at: www.azdeq.gov/environ/water/assessment/ambient.html

ADEQ Ambient Groundwater Reports

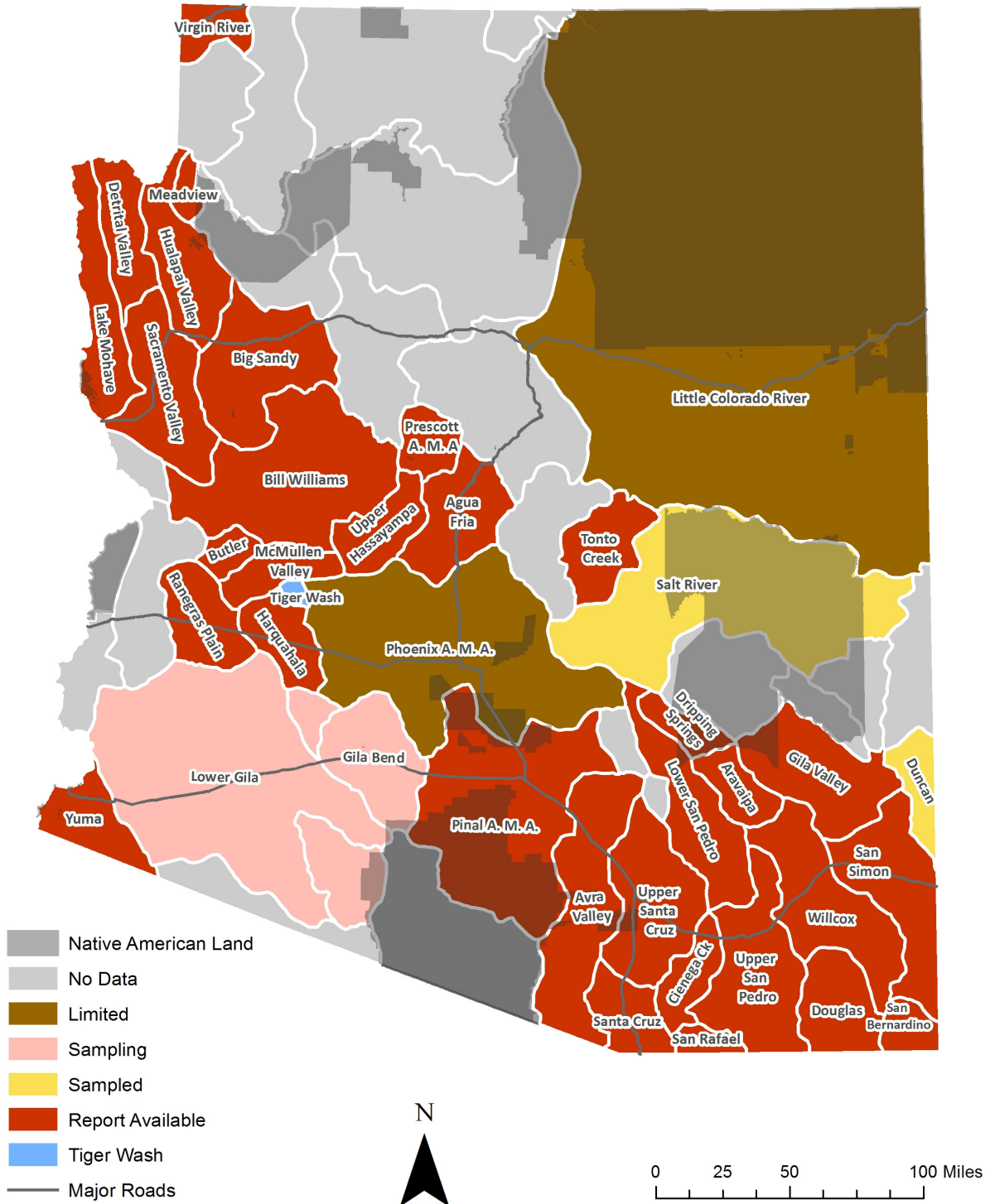


Table of Contents

Abstract	1
Introduction	2
Investigation Methods	2
Sample Collection	5
Laboratory Methods	5
Data Evaluation	11
Quality Assurance	11
Data Validation	11
Groundwater Sampling Results	13
Water Quality Standards / Guidelines	13
Analytical Results	13
Groundwater Composition	18
General Summary	18
Isotopes	25
Discussion	30
References	30
Appendices	
Appendix A – Data for Sample Sites, Tiger Wash basin, 2014.....	32
Appendix B – Groundwater Quality Data, Tiger Wash basin, 2014	32

Maps

ADEQ Ambient Monitoring Program Studies.....	V
Map 1. Tiger Wash Basin	3
Map 2. Sample Sites and Land Ownership	4
Map 3. Water Quality Standards.....	14
Map 4. Water Chemistry	19
Map 5. Total Dissolved Solids.....	21
Map 6. Nitrate	22
Map 7. Arsenic.....	23
Map 8. Radon and Geology	24

Tables

Table 1. Laboratory water methods and minimum reporting levels used in the study.....	5
Table 2. Summary results of split samples from the Accutest/Test America laboratories	12
Table 3. Sampled sites exceeding health-based water quality guidelines or Primary MCLs	15
Table 4. Summary statistics for groundwater quality data	16
Table 5. Summary of 18-Year Time Trend Sample Results at Headquarters Well (TIG-3).....	27
Table 6. Summary of 24-Year Time Trend Sample Results at Tiger Well (TIG-4)	29
Table 7. Summary of 20-Year Time Trend Sample Results at Tiger Well (TIG-4)	29

Diagrams

Diagram 1. Water chemistry piper plot	18
Diagram 2. Sodium-sulfate relationship	20
Diagram 3. Oxygen-18 – deuterium relationship	26
Diagram 4. Nitrogen-15 – nitrate relationship	26
Diagram 5. Nitrate concentrations over time in Old Headquarters well.....	27
Diagram 6. Chloride concentrations over time in Old Headquarters well	27

Figures

Figure 1. Tiger Wash	8
Figure 2. Eagle Eye Road	8
Figure 3. Mine Pump Well	9
Figure 4. Tiger Well	9
Figure 5. Headquarters Well.....	10
Figure 6. Pegrin Well.....	10
Figure 7. Pegrin Well notes	10
Figure 8. Little Horn Well	10

Abbreviations

amsl	above mean sea level
ac-ft	acre-feet
af/yr	acre-feet per year
ADEQ	Arizona Department of Environmental Quality
ADHS	Arizona Department of Health Services
ADWR	Arizona Department of Water Resources
ARRA	Arizona Radiation Regulatory Agency
AZGS	Arizona Geological Survey
As	arsenic
bls	below land surface
BLM	U.S. Department of the Interior Bureau of Land Management
°C	degrees Celsius
CI _{0.95}	95 percent Confidence Interval
Cl	chloride
EPA	U.S. Environmental Protection Agency
F	fluoride
Fe	iron
gpm	gallons per minute
GWPL	Groundwater Protection List active ingredient
HCl	hydrochloric acid
LLD	Lower Limit of Detection
Mn	manganese
MCL	Maximum Contaminant Level
ml	milliliter
msl	mean sea level
ug/L	micrograms per liter
um	micron
μS/cm	microsiemens per centimeter at 25° Celsius
mg/L	milligrams per liter
MRL	Minimum Reporting Level
ns	not significant
ntu	nephelometric turbidity unit
pCi/L	picocuries per liter
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
SAR	Sodium Adsorption Ratio
SDW	Safe Drinking Water
SC	Specific Conductivity
su	standard pH units
SO ₄	sulfate
TDS	Total Dissolved Solids
TKN	Total Kjeldahl Nitrogen
TIG	Tiger Wash groundwater basin
USGS	U.S. Geological Survey

Ambient Groundwater Quality of the Tiger Wash Basin: A 2014 Baseline Study

Abstract – In 2014, the Arizona Department of Environmental Quality (ADEQ) conducted a baseline groundwater quality study of the Tiger Wash basin in west-central Arizona. The small, remote basin comprises 74 square miles within Maricopa County and consists of a narrow valley bordered by rugged mountain ranges.⁵ Low-intensity livestock grazing and recreation are the predominant land uses. Within the basin, there are also small inactive mines and the Ambrosia Mill, which briefly processed manganese ore in the early 1960s.⁸ Land ownership consists of federal lands (97.4 percent) managed by the Bureau of Land Management (BLM), State Trust lands (2.3 percent) and private land (0.3 percent).^{4, 5} There are no incorporated communities within the basin, which had a population of less than 10 people in 2000.⁵

The basin is bounded on the north by the Harquahala Mountains and the Little Horn Mountains on the south. The small, shallow, alluvium-filled basin is drained by Tiger Wash which is a tributary of Centennial Wash. Tiger Wash heads in the northwest portion of the basin and flows south and west until exiting into the Harquahala basin shortly after crossing Eagle Eye Road.¹⁴ All washes in the basin are ephemeral and flow only after heavy precipitation except for an intermittent portion of Browns Canyon Wash within the Harquahala Mountains.¹⁴ Groundwater is used for stock and domestic purposes.

The main aquifer in the Tiger Wash basin is basin-fill alluvium that is composed of heterogeneous deposits of clay, silt, sand, and gravel that are less than 1,000 feet thick.¹⁴ Groundwater flow is to the northeast and southwest away from the center of the basin.¹⁴ The basin contains an estimated 700,000 to 2 million acre-feet of water to a depth of 1,200 feet below land surface. Natural recharge is estimated to be less than 1,000 acre-feet per year.⁵ Only a few low-yield wells used for stock purposes exist in the basin. Based on field reconnaissance, all known wells in the basin were sampled for the study.

Five wells were sampled; four were powered by windmills and one by a portable generator. Inorganic constituents and isotopes (oxygen, deuterium, and nitrogen) samples were collected at all five wells while radon (three samples) and radionuclides (two samples) were collected at selected sites.

Health-based, Primary Maximum Contaminant Levels (MCLs) are enforceable standards that define the maximum concentrations of constituents allowed in water supplied for drinking water purposes by a public water system and are based on a lifetime daily consumption of two liters.²⁹ Of the five sites sampled, three sites (60 percent) exceeded the federal arsenic Primary MCL of 0.01 milligram per Liter (mg/L) and one site exceeded the state arsenic standard of 0.05 mg/L. Only arsenic exceeded standards and appears to be naturally occurring caused by local lithology.

Aesthetics-based, Secondary MCLs are unenforceable guidelines that define the maximum constituent concentration that can be present in drinking water without an unpleasant taste, color, or odor.²⁹ Secondary MCLs were not exceeded at any of the five sites. Of the three sites sampled for radon, two sites (66 percent) exceeded the proposed 300 picocuries per liter standard but none exceeded the proposed 4,000 picocuries per liter standard.³⁰ The two sites at which radionuclide samples were collected did not have elevated concentrations of either gross alpha or uranium.

Groundwater is of calcium-bicarbonate chemistry and, based on pH, total dissolved solids, and hardness concentrations, is categorized as *slightly-alkaline*, *fresh*, and *hard*.^{10, 13} Most trace elements such as aluminum, antimony, beryllium, boron, cadmium, chromium, iron, lead, manganese, mercury, nickel, selenium, silver, and thallium were rarely – if ever - detected. Only arsenic, barium, copper, fluoride, strontium, and zinc were detected at more than 40 percent of the sites.

Oxygen and deuterium isotope values of the samples have been subject to evaporation and can be characterized as younger, enriched water. The enriched samples are similar to those collected from a small subset of wells, often located near bedrock areas, in other nearby western Arizona basins.²³ In contrast, most isotope samples in this region have depleted values that suggest that the majority of groundwater was recharged long ago (8,000 to 12,000 years) during cooler climatic conditions.^{11, 23, 24, 25, 26} Wells with enriched samples in other basins rarely exceeded water quality standards for arsenic but this commonly occurs in the Tiger Wash basin. Nitrogen isotope values suggest the source of nitrate is from natural soil organic matter in three samples and from animal waste in two samples.^{20, 22}

INTRODUCTION

Purpose and Scope

The Tiger Wash groundwater basin comprises approximately 74 square miles within Maricopa County in the west central portion of Arizona (Map 1).⁵ The Tiger Wash basin, which is the smallest officially designated groundwater basin in the state, is located about 75 miles northwest of Phoenix. There are no incorporated towns in the rural basin, which had an estimated population of less than 10 people in 2000.⁵ The basin is a small, shallow alluvium-filled valley bordered by mountain ranges. Groundwater is used for stock and domestic uses.

Sampling by the Arizona Department of Environmental Quality (ADEQ) Ambient Groundwater Monitoring program is authorized by legislative mandate in the Arizona Revised Statutes §49-225, specifically: *“...ongoing monitoring of waters of the state, including...aquifers to detect the presence of new and existing pollutants, determine compliance with applicable water quality standards, determine the effectiveness of best management practices, evaluate the effects of pollutants on public health or the environment, and determine water quality trends.”*³

Benefits of ADEQ Study – This study, which utilizes scientific sampling techniques and quantitative analyses, is designed to characterize regional groundwater quality conditions in the Tiger Wash basin.

Physical and Cultural Characteristics

Geography – The Tiger Wash basin is located within the Basin and Range physiographic province of central Arizona. The basin is drained by Tiger Wash and bordered by rugged mountains. Vegetation is composed of Lower Colorado River Valley and Arizona uplands Sonoran desert scrub with some Southwestern interior chaparral in the northwest of the basin.⁵

The basin is bounded on the north by the Harquahala Mountains and the Little Horn Mountains on the south. Elevations range from a maximum of approximately 2,724 feet above mean sea level (amsl) at Little Horn Mountain to a low of approximately 1,950 feet amsl where Tiger Wash exits into the Harquahala basin.

Land use in the basin is predominantly livestock grazing and recreational activities such as hiking, though there are several small, inactive mines and the former Ambrosia Mill. The latter property, located on private land, briefly processed manganese ore in 1960-

61 for the U.S. Department of Defense. The mill and equipment were later dismantled and sold. There remains, however, 150,000 tons of mill tailings having manganese and arsenic levels that are significantly above the Arizona non-residential soil remediation levels.⁸

All streams in the basin are ephemeral except for an intermittent stretch of Browns Canyon Wash, which is located in the Harquahala Mountains.⁵

Land Ownership - The Tiger Wash basin consists of federal land (97.4 percent) managed by the U.S. Bureau of Land Management (BLM), including a portion of the Harquahala Mountains Wilderness.⁷ The remainder of the basin is composed of State Trust lands (2.3 percent), and private lands (0.3 percent).^{4,5}

Climate – The Tiger Wash basin is in a semiarid climate characterized by hot, dry summers and mild winters. Precipitation amounts vary by elevation and range annually from 10 to 16 inches. Precipitation occurs predominantly as rain in either late summer, localized thunderstorms or, less often, as widespread, low intensity winter rain that rarely includes snow at higher elevations.⁵

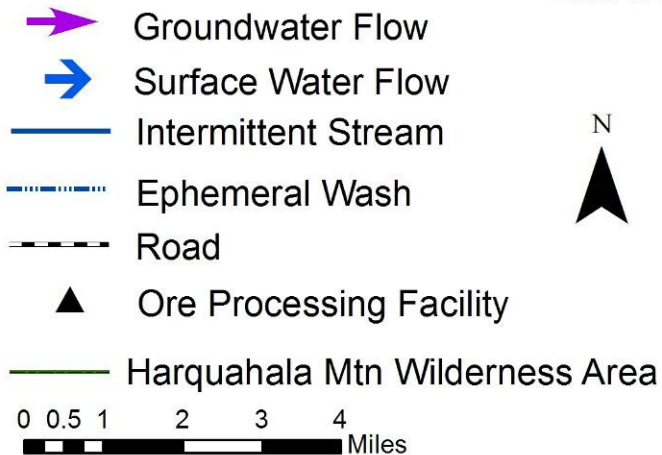
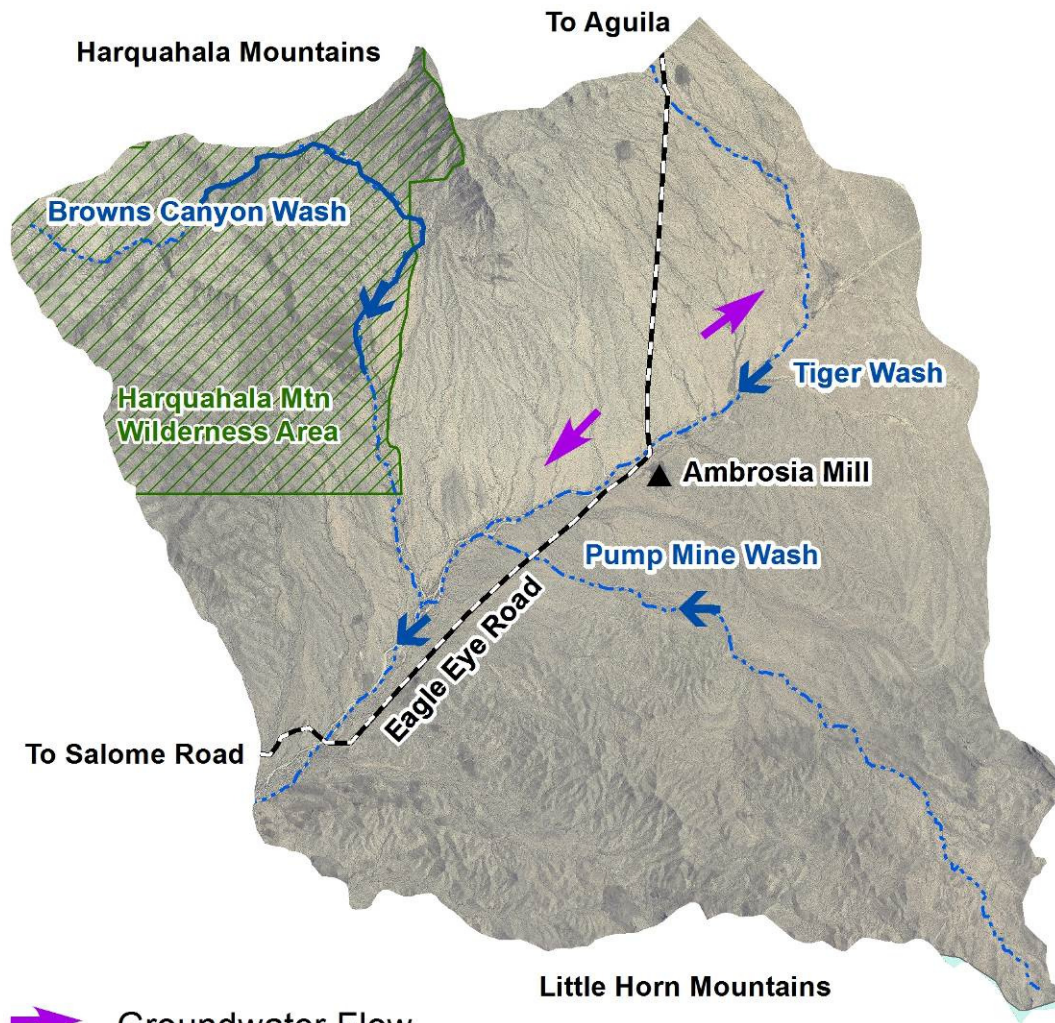
Groundwater - The main aquifer in the Tiger Wash basin is the basin-fill alluvium that is composed of heterogeneous deposits of clay, silt, sand, and gravel that are less than 1,000 feet thick.¹⁴ Groundwater flow is surmised to be to the northeast and southwest away from the center of the basin based on a very limited amount of data, raising the question of why this basin was originally delineated.¹⁴ The few wells in the basin are low yielding and are used for stock and domestic purposes.¹⁴ Natural recharge is less than 1,000 acre-feet (af) per year. There is an estimated 700,000 to 2 million af of water in storage to a depth of 1,200 below land surface (bls).⁵

INVESTIGATION METHODS

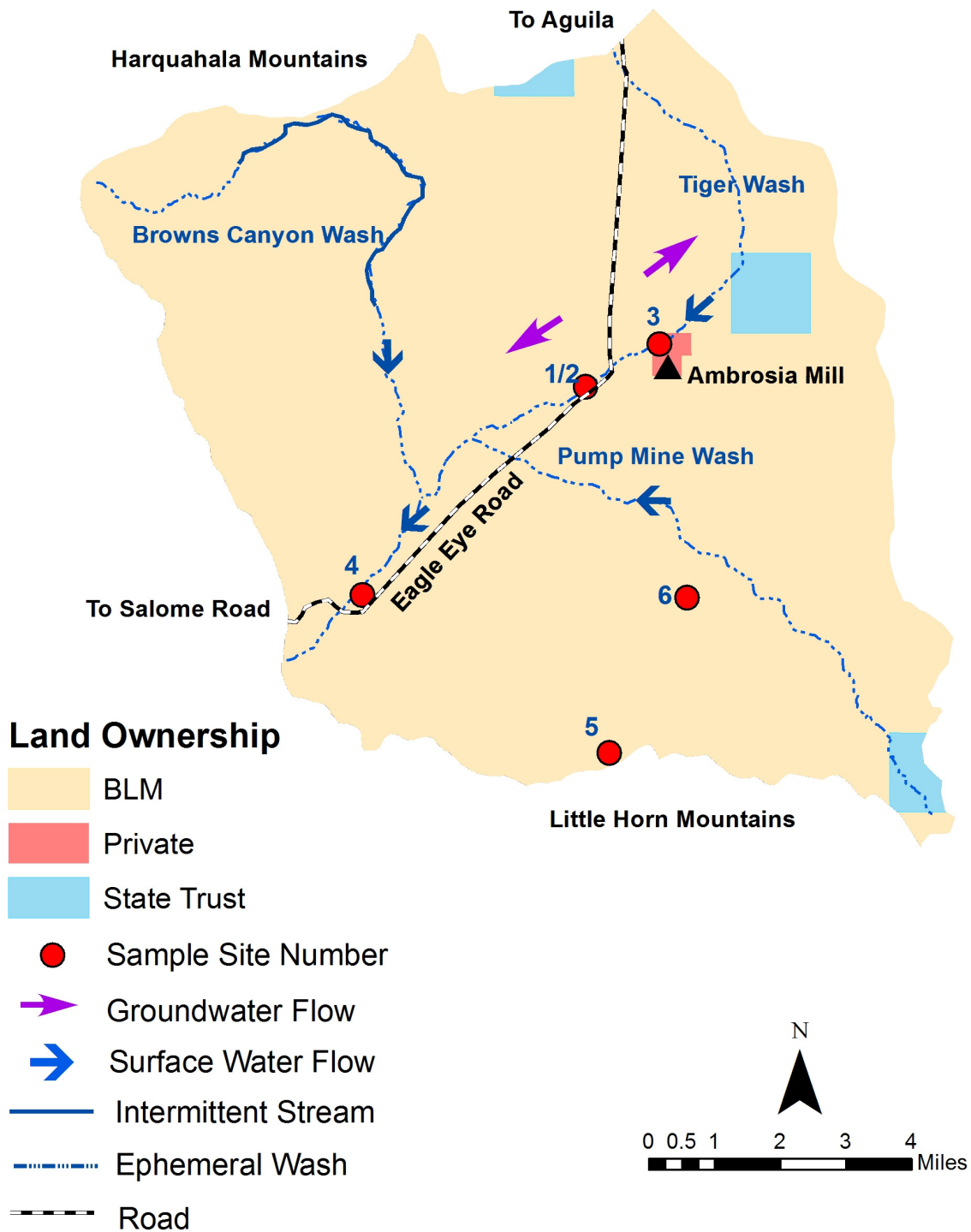
ADEQ collected samples from five wells to characterize regional groundwater quality in the Tiger Wash basin (Map 2). This is thought to be all of the active wells in the basin based on field reconnaissance. The following types of samples were collected:

- inorganic suites at five sites
- oxygen and deuterium isotopes at five sites
- nitrogen isotopes at five sites
- radon at three sites
- radionuclides at two sites

Map 1 - Tiger Wash Basin



Map 2 - Sample Sites and Land Ownership



No bacteria sampling was conducted because microbiological contamination problems in groundwater are often transient and subject to a variety of changing environmental conditions including soil moisture content and temperature.¹²

Five wells used for stock watering were sampled for the study. A well was considered suitable for sampling when the following conditions were met: the owner had given permission, a sampling point existed near the wellhead, and the well casing and surface seal appeared to be intact and undamaged.^{2,6}

Additional information on groundwater sample sites was compiled from the Arizona Department of Water Resources (ADWR) well registry and is available in Appendix A.⁵

Sample Collection

The sample collection methods for this study conformed to the *Quality Assurance Project Plan* (QAPP)² and the *Field Manual for Water Quality Sampling*.⁶ While these sources should be consulted as references to specific sampling questions, a brief synopsis of the procedures involved in collecting a groundwater sample is provided.

After obtaining permission from the well owner, the volume of water needed to purge the well three bore-hole volumes was calculated from well log and on-site information. Physical parameters—temperature, pH, and Specific Conductivity (SC)—were monitored every five minutes using a YSI multi-parameter instrument.

To assure obtaining fresh water from the aquifer, after three bore volumes had been pumped and physical parameter measurements had stabilized within 10 percent, a sample representative of the aquifer was collected from a point as close to the wellhead as possible.

In certain instances, it was not possible to purge three bore volumes. In these cases, at least one bore volume was evacuated and the physical parameters had stabilized within 10 percent. Sample bottles were labeled with a Tiger Wash identifier (TIG) and filled in the following order:

1. Radon
2. Inorganics
3. Radionuclide
4. Isotopes

Radon, a naturally occurring, intermediate breakdown from the radioactive decay of uranium-238 to lead-206, was collected in two unpreserved, 40 milliliter (ml) clear glass vials. Radon samples were filled to minimize volatilization and sealed so that no headspace remained.^{1,21}

The inorganic constituents were collected in three, one-liter polyethylene bottles. Samples to be analyzed for dissolved metals were filtered into bottles using a positive pressure filtering apparatus with a 0.45 micron (µm) pore size groundwater capsule filter and preserved with 5 ml nitric acid (70 percent). Samples to be analyzed for nutrients were preserved with 2 ml sulfuric acid (95.5 percent). Samples to be analyzed for other inorganic parameters were unpreserved.^{1,21}

Radiochemistry samples were collected in two collapsible 4-liter plastic containers and preserved with 5 ml nitric acid to reduce the pH below 2.5 su.¹

Oxygen and hydrogen isotope samples were collected in a 250 ml polyethylene bottle with no preservative.²⁶ Nitrogen isotope samples were collected in a 500 ml polyethylene bottle and filled ¾ full to allow room for expansion when frozen.²⁸

All samples were kept at 4° Celsius with ice in an insulated cooler, with the exception of the oxygen and hydrogen isotope samples.²⁸ Nitrogen samples were frozen upon returning from the field and shipped in dry ice to the laboratory.²⁸ Chain of custody procedures were followed in sample handling. Samples for this study were collected during two field trips conducted in early 2014.

Laboratory Methods

Inorganic analyses for the study were analyzed by Accutest Northern California Laboratory in San Jose, California. A complete listing of inorganic parameters, including laboratory method and Minimum Reporting Level (MRL) for each laboratory is provided in Table 1.

Radionuclide and radon analyses were conducted by Radiation Safety Engineering, Inc. Laboratory in Chandler, Arizona.

Isotope samples were analyzed by the Laboratory of Isotope Geochemistry at the University of Arizona in Tucson, Arizona.

Table 1. Laboratory Water Methods and Minimum Reporting Levels Used in the Study

Constituent	Instrumentation	Test America / Accutest Water Method	Test America/ Accutest Minimum Reporting Level
Physical Parameters and General Mineral Characteristics			
Alkalinity	Electrometric Titration	SM18 2320B	6 / 5
SC (µS/cm)	Electrometric	SM 2510 B / EPA 120.1	2 / 1
Hardness	Titrimetric, EDTA	SM 2340 C	- / -
Hardness	Calculation	SM 2340 B	--
pH (su)	Electrometric	SM 4500 H-B	0.1
TDS	Gravimetric	SM 2540C	10
Turbidity (NTU)	Nephelometric	EPA 180.1 / SM 2130B	0.2 / 0.5
Major Ions			
Calcium	ICP-AES	EPA 200.7	2 / 5
Magnesium	ICP-AES	EPA 200.7	0.25 / 5
Sodium	ICP-AES	EPA 200.8	2 / 0.50
Potassium	Flame AA	EPA 200.8	2 / 0.5
Bicarbonate	Calculation	Calculation / SM 2320 B	2 / 5
Carbonate	Calculation	Calculation / SM 2320 B	2 / 5
Chloride	Potentiometric Titration	EPA 300	2 / 0.5
Sulfate	Colorimetric	EPA 300	2 / 0.5
Nutrients			
Nitrate as N	Colorimetric	EPA 353.2 / EPA 300	0.1 / 0.25
Nitrite as N	Colorimetric	EPA 353.2 / EPA 300	0.1 / 0.25
Ammonia	Colorimetric	EPA 350.3 / SM 4500	0.5 / 1.0
TKN	Colorimetric	SM 4500	1.3 / 0.2
Total Phosphorus	Colorimetric	SM 4500	0.1 / 0.02

All units are mg/L except as noted
Source ^{1, 21}

Table 1. Laboratory Water Methods and Minimum Reporting Levels Used in the Study-Continued

Constituent	Instrumentation	Test America / Accutest Water Method	Test America/ Accutest Minimum Reporting Level
Trace Elements			
Aluminum	ICP-AES	EPA 200.7	0.2 / 0.2
Antimony	Graphite Furnace AA	EPA 200.8	0.003 / 0.004
Arsenic	Graphite Furnace AA	EPA 200.8	0.001 / 0.004
Barium	ICP-AES	EPA 200.7 / EPA 200.8	0.01 / 0.002
Beryllium	Graphite Furnace AA	EPA 200.8 / EPA 200.7	0.001 / 0.005
Boron	ICP-AES	EPA 200.7	0.2 / 0.10
Cadmium	Graphite Furnace AA	EPA 200.8	0.001 / 0.002
Chromium	Graphite Furnace AA	EPA 200.7 / EPA 200.8	0.01 / 0.002
Copper	Graphite Furnace AA	EPA 200.7 / EPA 200.8	0.01 / 0.004
Fluoride	Ion Selective Electrode	SM 4500 F-C / EPA 300	0.4 / 0.10
Iron	ICP-AES	EPA 200.7	0.05 / 0.20
Lead	Graphite Furnace AA	EPA 200.8	0.001 / 0.002
Manganese	ICP-AES	EPA 200.7	0.01 / 0.15
Mercury	Cold Vapor AA	EPA 245.1	0.0002
Nickel	ICP-AES	EPA 200.7	0.01 / 0.005
Selenium	Graphite Furnace AA	EPA 200.8	0.002 / 0.004
Silver	Graphite Furnace AA	EPA 200.7 / EPA 200.8	0.01 / 0.002
Strontium	ICP-AES	EPA 200.7	0.1 / 0.01
Thallium	Graphite Furnace AA	EPA 200.8	0.001 / 0.002
Zinc	ICP-AES	EPA 200.7	0.05 / 0.02
Radionuclides			
Gross alpha	Gas flow counter	EPA 900.0	varies
Radium 226	Gas flow counter	EPA 903.0	varies
Radium 228	Gas flow counter	EPA 904.0	varies
Radon	Liquid scantill. counter	EPA 913.1	varies
Uranium	Kinetic phosphorimeter	EPA Laser Phosphorimetry	varies

All units are mg/L Source ^{1, 21}



Figure 1 –The basin is drained by Tiger Wash, an ephemeral waterway that flows only in response to major precipitation events. The wash is shown here crossing Eagle Eye Road.



Figure 2 – Looking north along Eagle Eye Road from a former loading site for ore from the nearby Black Nugget and Black Queen mines. More than 97 percent of the basin consists of federally owned land managed by the Bureau of Land Management that is used for low intensity livestock grazing and recreation.⁵



Figure 3 – A generator powers the submersible pump in Mine Pump well. Water from the well is piped to a nearby water tank and distributed to troughs for livestock and wildlife use. A split sample (TIG-1/2) was collected from the well.



Figure 4 –Tiger well is photographed from the nearby corral, in the background are the Harquahala Mountains. The sample collected from the windmill met all water quality standards except for arsenic.



Figure 5 – Headquarters well is located on a small enclave of private land in the basin. Formerly powered by a pump jack, the sample (TIG-3) collected from the windmill met all water quality standards.

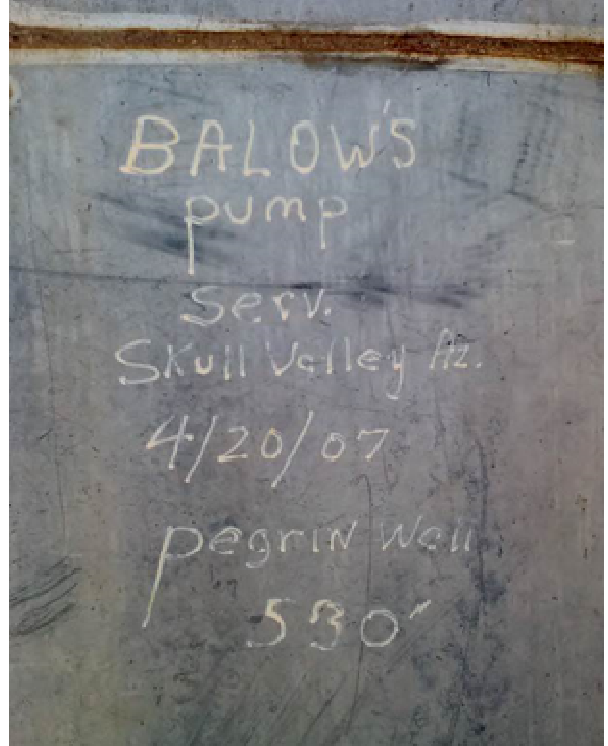


Figure 7 – The “graffiti” on Pegrin well’s adjacent water tank is actually valuable hydrologic notes left by Balow’s Pump when the company serviced the well.



Figure 6 – ADEQ’s Elizabeth Boettcher collects a sample (TIG-6) from Pegrin well. The well was temporarily powered by a pump jack to keep up with livestock water demands because of calm winter winds.



Figure 8 – The water tank supplied by Little Horn well was full when a sample (TIG-5) was collected in February 2014. Overflow from the windmill supports a small riparian area adjacent to the tank.

DATA EVALUATION

Quality Assurance

Quality-assurance (QA) procedures were followed and quality-control (QC) samples were collected to quantify data bias and variability for the Tiger Wash basin study. The design of the QA/QC plan was based on recommendations included in the *Quality Assurance Project Plan (QAPP)* and the *Field Manual for Water Quality Sampling*.^{2, 6} The QC inorganic samples collected for this study include one split.

Split Samples – Split samples are identical sets of samples collected from the same source at the same time that are submitted to two different laboratories to check for laboratory differences.⁶ One inorganic split sample was collected and distributed between the Accutest and Test America labs. The analytical results were evaluated by examining the variability in constituent concentrations in terms of absolute levels and as the percent difference.

Analytical results indicate that of the 41 constituents examined, 18 had concentrations above MRLs for both the Accutest and Test America laboratories. The maximum variation between constituents was below seven percent except for turbidity (Table 2).

Based on the results of blank, duplicate, split, time-trend samples collected for this study, no significant QA/QC problems were apparent with the study.

Data Validation

The analytical work for this study was subjected to four QA/QC correlations and considered valid based on the following results.¹⁵

Cation/Anion Balances – In theory, water samples exhibit electrical neutrality. Therefore, the sum of milliequivalents per liter (meq/L) of cations should equal the sum of meq/L of anions. However, this neutrality rarely occurs due to unavoidable variation inherent in all water quality analyses. Still, if the cation/anion balance is found to be within acceptable

limits, it can be assumed there are no gross errors in concentrations reported for major ions.¹⁵

Overall, cation/anion meq/L balances of Tiger Wash basin samples were significantly correlated (regression analysis, $p \leq 0.01$). Of the five samples, all were within +/-11 percent and four samples were within +/- 5 percent. Three samples had low cation/high anion sums; two samples had high cation/low anion sums.

SC/TDS – The SC-lab and Total Dissolved Solids (TDS) concentrations measured by contract laboratories were significantly correlated as were SC-field and TDS concentrations (regression analysis, $r = 0.97$, $p \leq 0.01$). The TDS concentration in mg/L should be from 0.55 to 0.75 times the SC in $\mu\text{S/cm}$ for groundwater up to several thousand TDS mg/L.¹⁵

Groundwater high in bicarbonate and chloride will have a multiplication factor near the lower end of this range; groundwater high in sulfate may reach or even exceed the higher factor. The relationship of TDS to SC becomes undefined with very high or low concentrations of dissolved solids.¹⁵

SC – The SC measured in the field at the time of sampling was significantly correlated with the SC measured by contract laboratories (regression analysis, $r = 0.99$, $p \leq 0.01$).

pH – The pH values measured in the field using a YSI meter at the time of sampling were significantly correlated with laboratory pH values (regression analysis, $r = 0.87$, $p \geq 0.01$).

Based on the results of blank, duplicate, and split samples collected for this study, no significant QA/QC problems were apparent with the study.

Table 2. Summary Results of Split Sample between Accutest / Test America Laboratories

Constituents	Number of Split Sites	Difference in Percent	Difference in Concentration
Physical Parameters and General Mineral Characteristics			
Alkalinity, total	1	4 %	18
SC (µS/cm)	1	0 %	2
Hardness	1	3 %	12
pH (su)	1	1 %	0.2
TDS	1	7 %	41
Turbidity	1	13 %	0.7
Major Ions			
Calcium	1	1 %	1
Magnesium	1	3 %	1.2
Sodium	1	4 %	1.5
Potassium	1	4 %	0.16
Chloride	1	3 %	0.3
Sulfate	1	3 %	0.4
Nutrients			
Nitrate as N	1	3 %	0.2
Trace Elements			
Arsenic	1	1 %	0.0001
Barium	1	1 %	0.0008
Fluoride	1	3 %	0.006
Strontium	1	3 %	0.045
Zinc	1	7 %	0.21

All units are mg/L except as noted.

GROUNDWATER SAMPLING RESULTS

Water Quality Standards/Guidelines

The ADEQ ambient groundwater program characterizes regional groundwater quality. An important determination ADEQ makes concerning the collected samples is how the analytical results compare to various drinking water quality standards. ADEQ used three sets of drinking water standards that reflect the best current scientific and technical judgment available to evaluate the suitability of groundwater in the basin for drinking water use:

- Federal Safe Drinking Water Act (SDWA) Primary Maximum Contaminant Levels (MCLs). These enforceable health-based standards establish the maximum concentration of a constituent allowed in water supplied by public systems.²⁹
- State of Arizona Aquifer Water Quality Standards. These apply to aquifers that are classified for drinking water protected use. All aquifers within Arizona are currently classified and protected for drinking water use. These enforceable state standards are identical to the federal Primary MCLs except for arsenic which is at 0.05 mg/L compared with the federal Primary MCL of 0.01 mg/L and uranium with a federal Primary MCL of 30 ug/L.³
- Federal SDW Secondary MCLs. These non-enforceable aesthetics-based guidelines define the maximum concentration of a constituent that can be present without imparting unpleasant taste, color, odor, or other aesthetic effects on the water.²⁹

Health-based drinking water quality standards (such as Primary MCLs) are based on the lifetime consumption (70 years) of two liters of water per day and, as such, are chronic rather than acute standards.²⁹ Exceedances of specific constituents for each groundwater site is found in Appendix B.

Overall Results – Of the five sites sampled in the Tiger Wash study, two sites (40 percent) met all health-based and aesthetics-based, water quality

standards (excluding the proposed radon standard discussed below).

Of the five sites sampled in the Tiger Wash study, health-based water quality standards were exceeded at three sites (60 percent). Constituents above Primary MCLs are arsenic at all three sites.

Inorganic Constituent Results - Of the five sites sampled for the full suite of inorganic constituents (excluding radionuclide sample results) in the Tiger Wash study, two sites (40 percent) met all health-based and aesthetics-based, water quality standards.

Health-based Primary MCL water quality standards were exceeded at three of the five sites (Map 3; Table 3). Arsenic was the only inorganic constituent that exceeded a Primary MCL and was exceeded at the federal standard at three of the five sites and the state standard at one site. Potential impacts of these Primary MCL exceedances are given in Table 3.

Aesthetics-based Secondary MCL water quality guidelines were not exceeded at any of the five sites.

Radionuclide Results - Of the two sites sampled for gross alpha and uranium, neither one exceeded the respective health-based Primary MCL water quality standards

Radon Results - Of the three sites sampled for radon, none exceeded the proposed 4,000 picocuries per liter (pCi/L) standard that would apply if Arizona establishes an enhanced multimedia program to address the health risks from radon in indoor air. Two sites exceeded the proposed 300 pCi/L standard (Table 3) that would apply if Arizona doesn't develop a multimedia program.³⁰

Analytical Results

Analytical inorganic and radiochemistry results of the Tiger Wash sample sites are summarized (Table 4) using the following indices: MRLs, number of sample sites over the MRL, upper and lower 95 percent confidence intervals (CI_{95%}), median, and mean. Confidence intervals are a statistical tool which indicates that 95 percent of a constituent's population lies within the stated confidence interval.³² Specific constituent information for each sampled groundwater site is in Appendix B.

Map 3 - Water Quality Standards

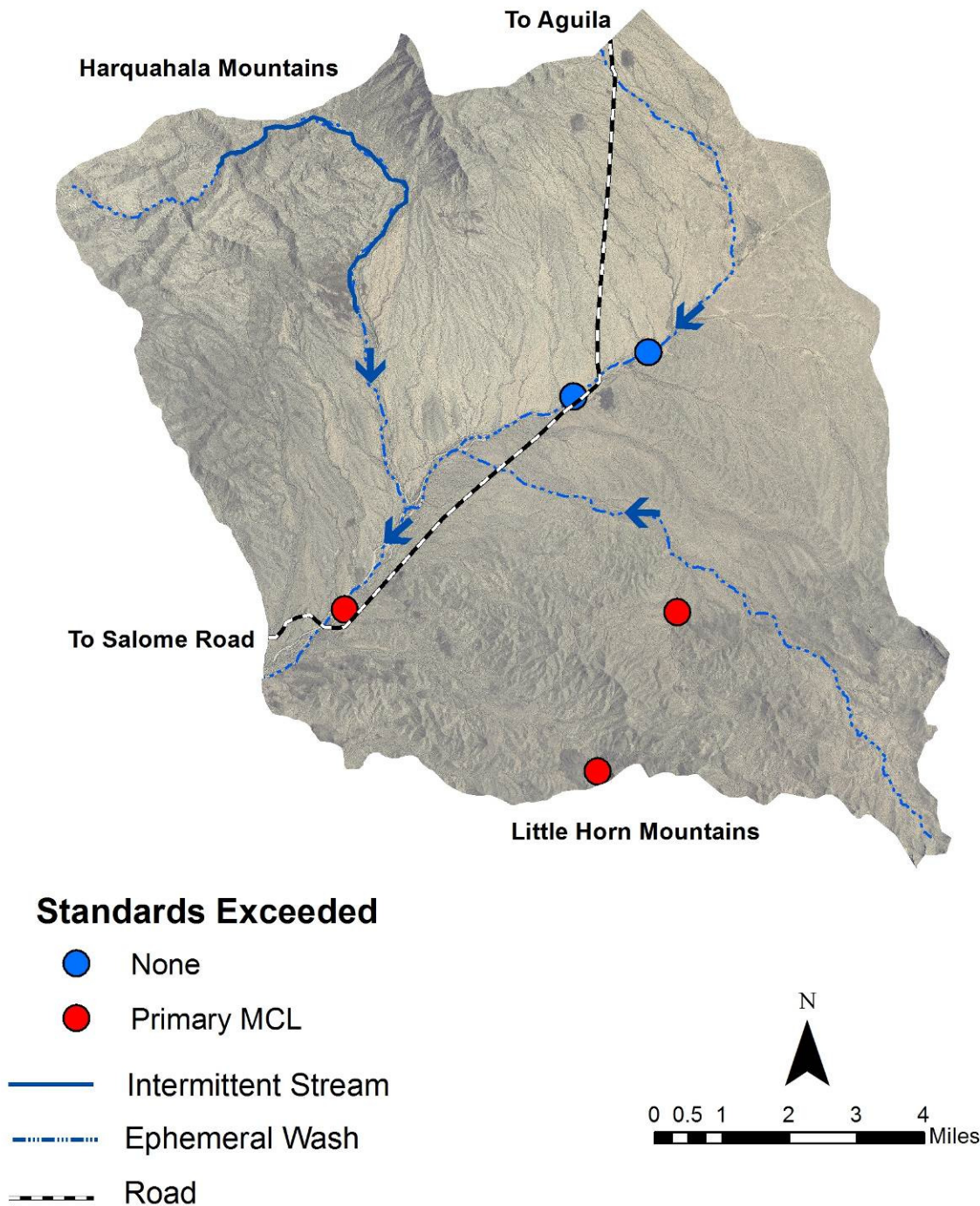


Table 3. Sampled Sites Exceeding Health-based Water Quality Standards or Primary MCLs

Constituent	Primary MCL	Number of Sites Exceeding Primary MCL	Highest Concentration	Potential Health Effects of MCL Exceedances *
Nutrients				
Nitrite (NO ₂ -N)	1.0	0	-	-
Nitrate (NO ₃ -N)	10.0	0	-	-
Trace Elements				
Antimony (Sb)	0.006	0	-	-
Arsenic (As)	0.01	3	0.0602	dermal and nervous system toxicity
Arsenic (As)	0.05	1	0.0602	dermal and nervous system toxicity
Barium (Ba)	2.0	0	-	-
Beryllium (Be)	0.004	0	-	-
Cadmium (Cd)	0.005	0	-	-
Chromium (Cr)	0.1	0	-	-
Copper (Cu)	1.3	0	-	-
Fluoride (F)	4.0	0	-	-
Lead (Pb)	0.015	0	-	-
Mercury (Hg)	0.002	0	-	-
Nickel (Ni)	0.1	0	-	-
Selenium (Se)	0.05	0	-	-
Thallium (Tl)**	0.002	0	-	-
Radionuclide Constituents				
Gross Alpha	15	0	-	-
Radon **	300	2	524	cancer
Radon **	4,000	0	-	-
Uranium	30	0	-	-

All units are mg/L except gross alpha, radium-226+228 and radon (pCi/L), and uranium (ug/L).

* Health-based drinking water quality standards are based on a lifetime consumption of two liters of water per day over a 70-year life span.²⁹

** Proposed EPA Safe Drinking Water Act standards for radon in drinking water.³⁰

Table 4. Summary Statistics for Groundwater Quality Data

Constituent	Minimum Reporting Limit (MRL)*	# of Samples / Samples Over MRL	Median	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
Physical Parameters						
Temperature (°C)	0.1	5 / 5	22.3	19.5	22.4	25.3
pH-field (su)	0.01	5 / 5	7.64	7.37	7.64	7.91
pH-lab (su)	0.01	5 / 5	7.70	7.22	7.70	8.18
Turbidity (ntu)	0.20 / 0.50	5 / 2	> 50 percent of data below MRL			
General Mineral Characteristics						
T. Alkalinity	6.0 / 5.0	5 / 5	228	176	215	253
SC-field (µS/cm)	N/A	5 / 5	472	362	458	554
SC-lab (µS/cm)	2.0 / 1.0	5 / 5	495	328	460	591
Hardness-lab	-	5 / 5	286	229	284	338
TDS-field	-	5 / 5	307	236	293	349
TDS-lab	20 / 10	5 / 5	286	229	284	338
Major Ions						
Calcium	2 / 5	5 / 5	44	23	42	62
Magnesium	0.25 / 5.0	5 / 5	19	14	21	29
Sodium	2 / 0.5	5 / 5	23	10	30	50
Potassium	2.0 / 0.5	5 / 5	2.1	1.2	2.0	2.8
Bicarbonate	6.0 / 5.0	5 / 5	278	215	262	308
Carbonate	6.0 / 5.0	5 / 0	> 50 percent of data below MRL			
Chloride	20 / 0.5	5 / 5	9	0	15	32
Sulfate	20 / 0.5	5 / 5	8	- 2	13	28
Nutrients						
Nitrate (as N)	0.1 / 0.25	5 / 5	3.4	1.7	3.9	6.1
Nitrite (as N)	0.1 / 0.25	5 / 0	> 50% of data below MRL			
TKN	1.3 / 0.2	5 / 2	> 50% of data below MRL			
Ammonia	0.5 / 1.0	5 / 0	> 50% of data below MRL			
T. Phosphorus	0.1 / .02	5 / 3	0.22	0.07	0.22	0.37

Table 4. Summary Statistics for Groundwater Quality Data—Continued

Constituent	Minimum Reporting Limit (MRL)*	# of Samples / Samples Over MRL	Median	Lower 95% Confidence Interval	Mean	Upper 95% Confidence Interval
Trace Elements						
Aluminum	0.2	5 / 0		> 50% of data below MRL		
Antimony	0.003 / 0.004	5 / 0		> 50% of data below MRL		
Arsenic	0.001 / 0.004	5 / 4	0.012	- 0.009	0.021	0.051
Barium	0.01 / 0.002	5 / 4	0.034	- 0.007	0.33	0.074
Beryllium	0.001 / 0.005	5 / 0		> 50% of data below MRL		
Boron	0.2 / 0.1	5 / 2		> 50% of data below MRL		
Cadmium	0.001 / 0.002	5 / 0		> 50% of data below MRL		
Chromium	0.01 / 0.002	5 / 2		> 50% of data below MRL		
Copper	0.01 / 0.004	5 / 3	0.004	- 0.001	0.006	0.013
Fluoride	0.4 / 0.1	5 / 5	0.3	0.0	0.4	0.8
Iron	0.05 / 0.2	5 / 0		> 50% of data below MRL		
Lead	0.001 / 0.002	5 / 0		> 50% of data below MRL		
Manganese	0.01 / 0.15	5 / 1		> 50% of data below MRL		
Mercury	0.0002	5 / 0		> 50% of data below MRL		
Nickel	0.01 / 0.005	5 / 0		> 50% of data below MRL		
Selenium	0.002 / 0.004	5 / 0		> 50% of data below MRL		
Silver	0.01 / 0.002	5 / 0		> 50% of data below MRL		
Strontium	0.1 / 0.01	5 / 5	0.7	0.4	0.8	1.2
Thallium	0.001 / 0.002	5 / 0		> 50% of data below MRL		
Zinc	0.005 / 0.02	5 / 5	0.3	0.1	0.4	0.8
Radionuclide						
Gross Alpha**	Varies	2 / 2	4	- 22	4	30
Uranium**	Varies	2 / 2	3	- 13	3	19
Radon **	Varies	3 / 3	319	- 131	332	795
Isotopes						
Oxygen-18 ***	Varies	5 / 5	-8.1	-8.7	-7.9	-7.1
Deuterium ***	Varies	5 / 5	-56.0	-59.4	-55.8	-52.2
Nitrogen ***	Varies	5 / 5	4.5	0.6	8.3	16.0

* = Test America / Accutest MRL

All units mg/L except where noted: ** - (pCi/L) or *** - 0/00

GROUNDWATER COMPOSITION

General Summary

The water chemistry at the five sample sites in the Tiger Wash basin are all calcium-bicarbonate (Diagram 1 – middle figure) (Map 4). The dominant

cation was calcium at two sites, magnesium at two sites, and one site was mixed (Diagram 1 – left figure). The dominant anion was bicarbonate at five sites (Diagram 1 – right figure).

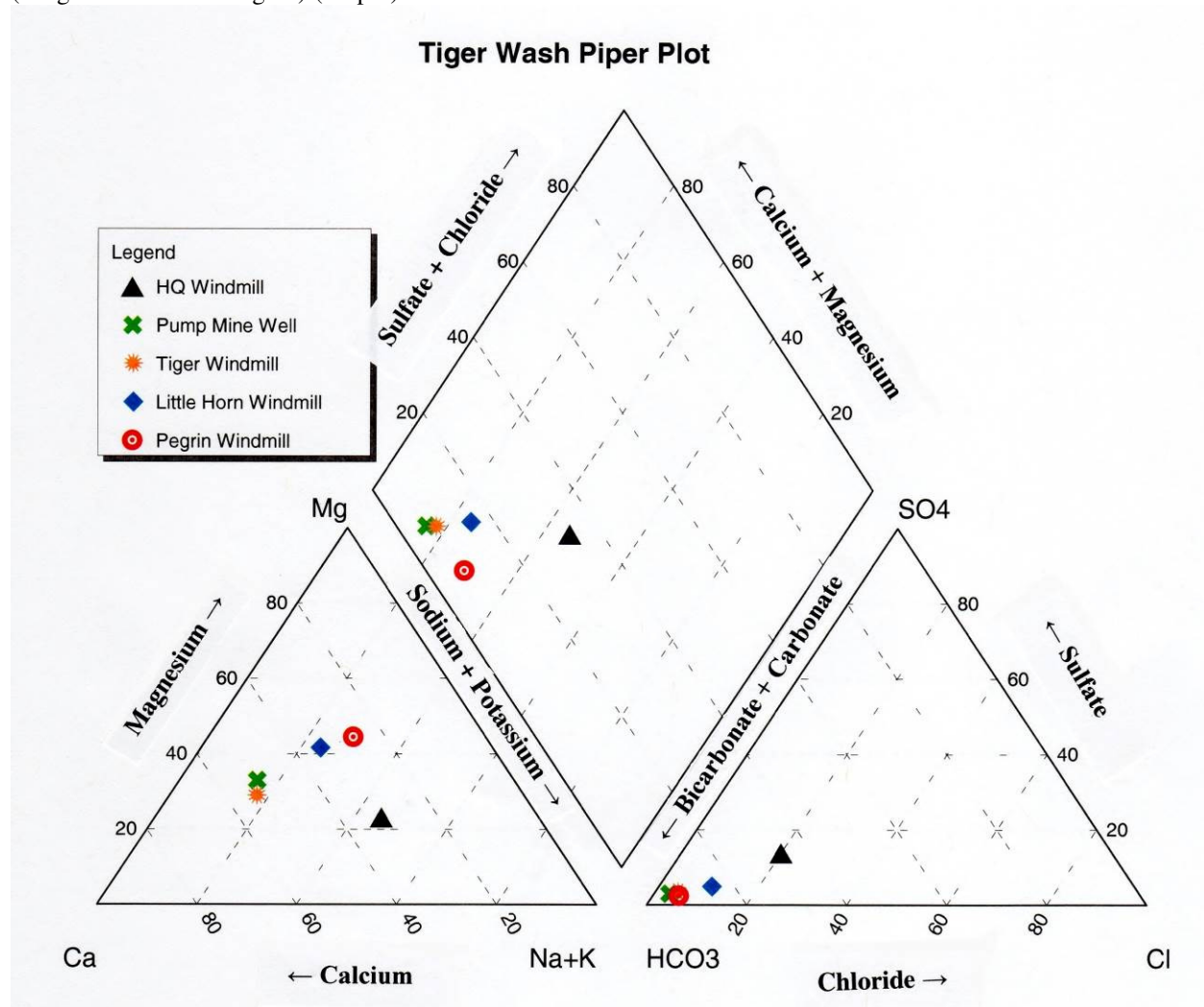
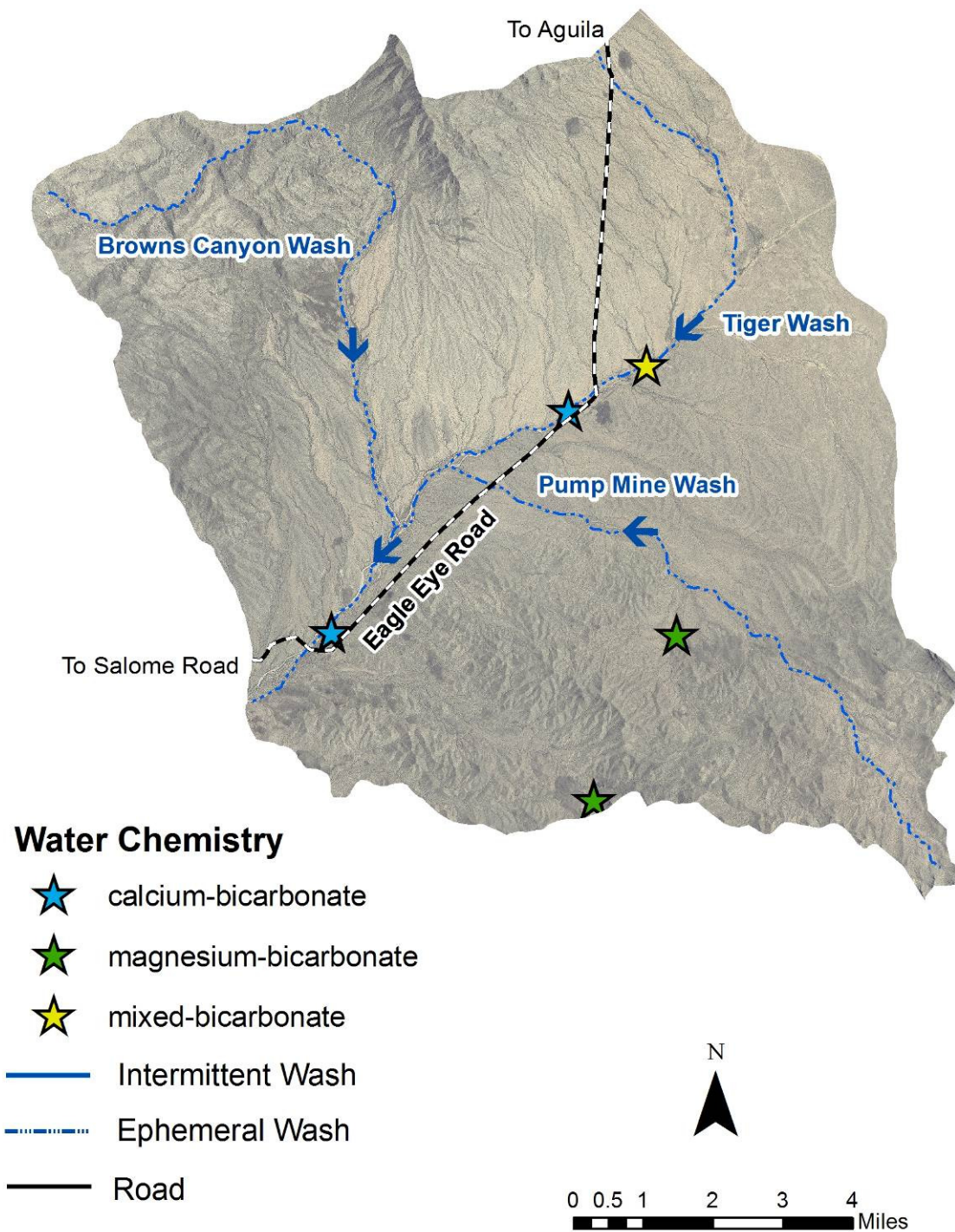


Diagram 1 – Samples collected in the Tiger Wash basin are predominantly of calcium/magnesium-bicarbonate chemistry which is reflective of recently recharged groundwater.¹⁹

Map 4 - Water Chemistry



At all five sites, levels of pH-field were *slightly alkaline* (above 7 su).¹³

TDS concentrations were considered *fresh* (below 999 mg/L) at five sites (Map 5).¹³

Hardness concentrations were *moderately hard* (75 – 150 mg/L) at one site and *hard* (150 – 300 mg/L) at four sites.¹⁰

Nitrate (as nitrogen) concentrations at most sites may have been influenced by human activities according to a prominent nationwide USGS study.²² Nitrate concentrations were divided into natural background (no sites at < 0.2 mg/L), may or may not indicate human influence (two sites at 0.2 – 3.0 mg/L), may result from human activities (three sites at 3.0 – 10 mg/L (Map 6)).¹⁷ This general classification system, however, may not appear to apply to Sonoran desert areas. Further analysis of nitrate concentrations is provided in the nitrogen isotope analysis section.

Most trace elements such as aluminum, antimony, beryllium, boron, cadmium, chromium, iron, lead, manganese, mercury, nickel, selenium, silver, and thallium were rarely – if ever - detected. Only arsenic (Map 7), barium, copper, fluoride, strontium, and zinc were detected at more than 40 percent of the sites.

The groundwater at each sample site was assessed as to its suitability for irrigation use based on salinity and sodium hazards. Excessive levels of sodium are known to cause physical deterioration of the soil and vegetation. Irrigation water may be classified using SC and the Sodium Adsorption Ratio (SAR) in conjunction with one another.³¹ Groundwater sites in the Tiger Wash basin all have a “C2-S1” irrigation classification that indicates samples have a “low” sodium hazard and a “medium” salinity hazard.

TDS concentrations are best predicted among major ions by sodium concentrations (standard coefficient = 0.78), among cations by sodium concentrations (standard coefficient = 0.60) and among anions, by sulfate concentrations (standard coefficient = 0.60) (multiple regression analysis, $p \leq 0.01$).

The three sites sampled for radon were collected from wells in three different geologic categories: alluvium, sedimentary, and volcanic (Map 8). The samples from the wells located in alluvium and volcanic geology exceeded the proposed 300 pCi/L standard that would apply if Arizona doesn't develop a multimedia program.³⁰

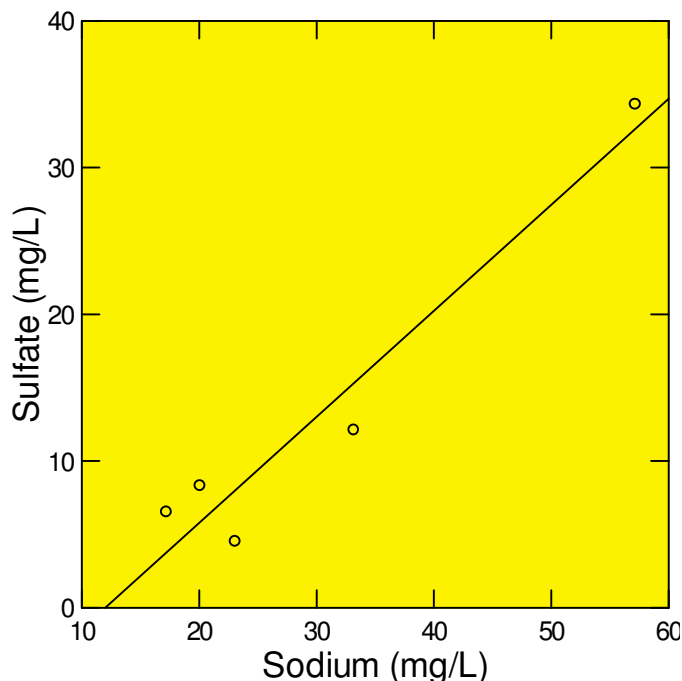
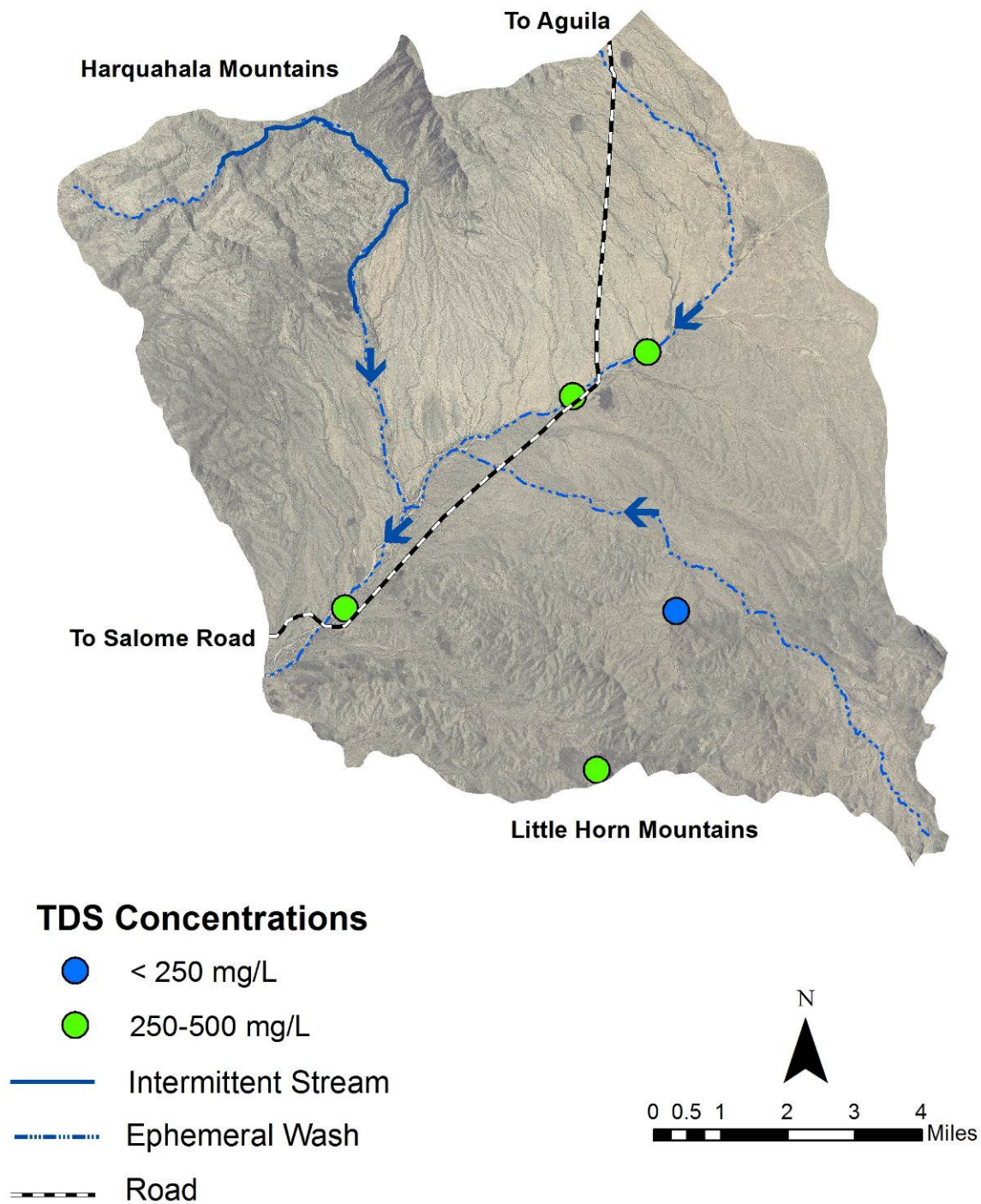
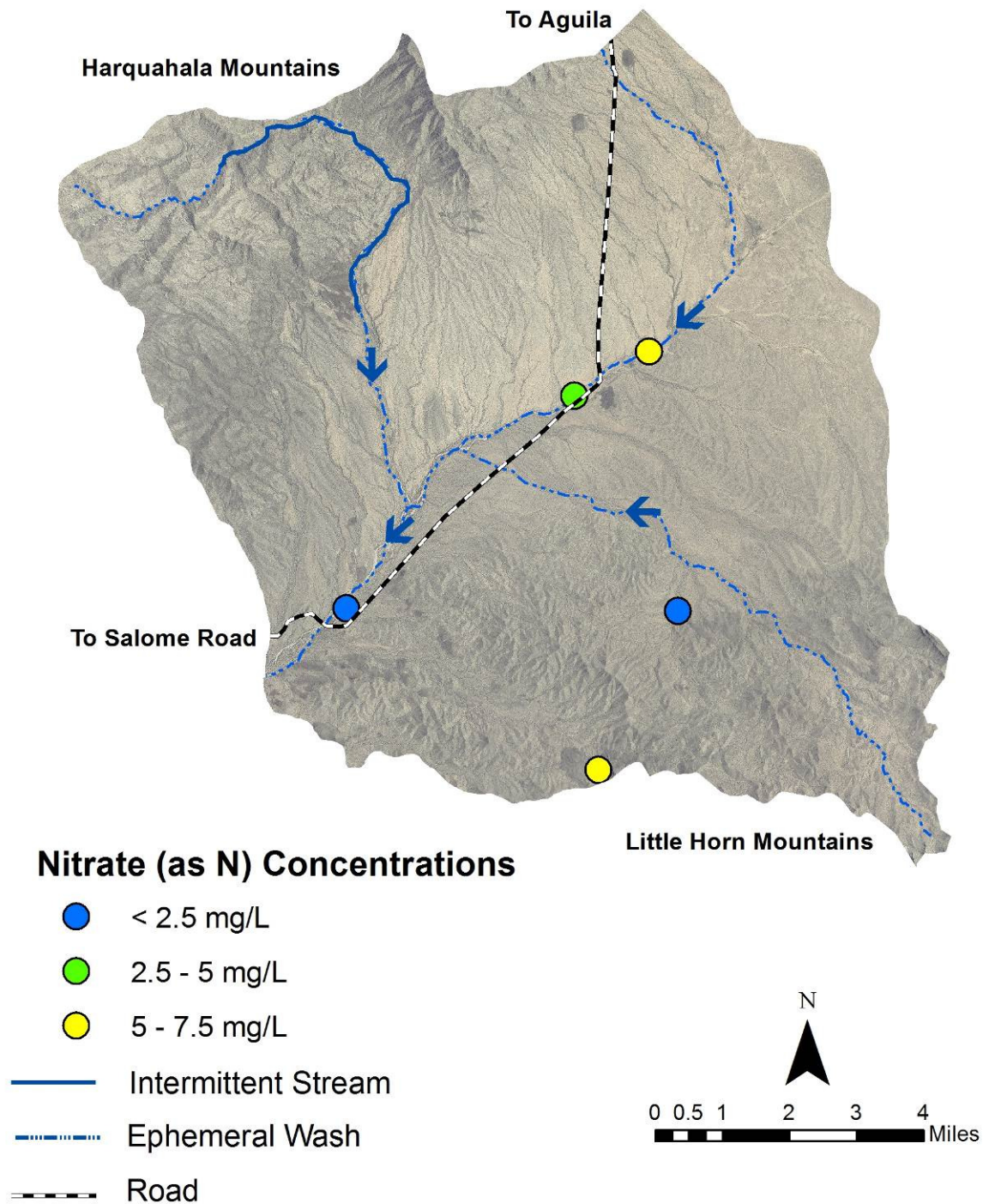


Diagram 2 – The cation and anion that best predict TDS concentrations, sodium and sulfate, are significantly positively correlated (regression analysis, $p \leq 0.01$). This relationship is described by the regression equation: $y = 1.3x + 13.2$ ($r = 0.97$).

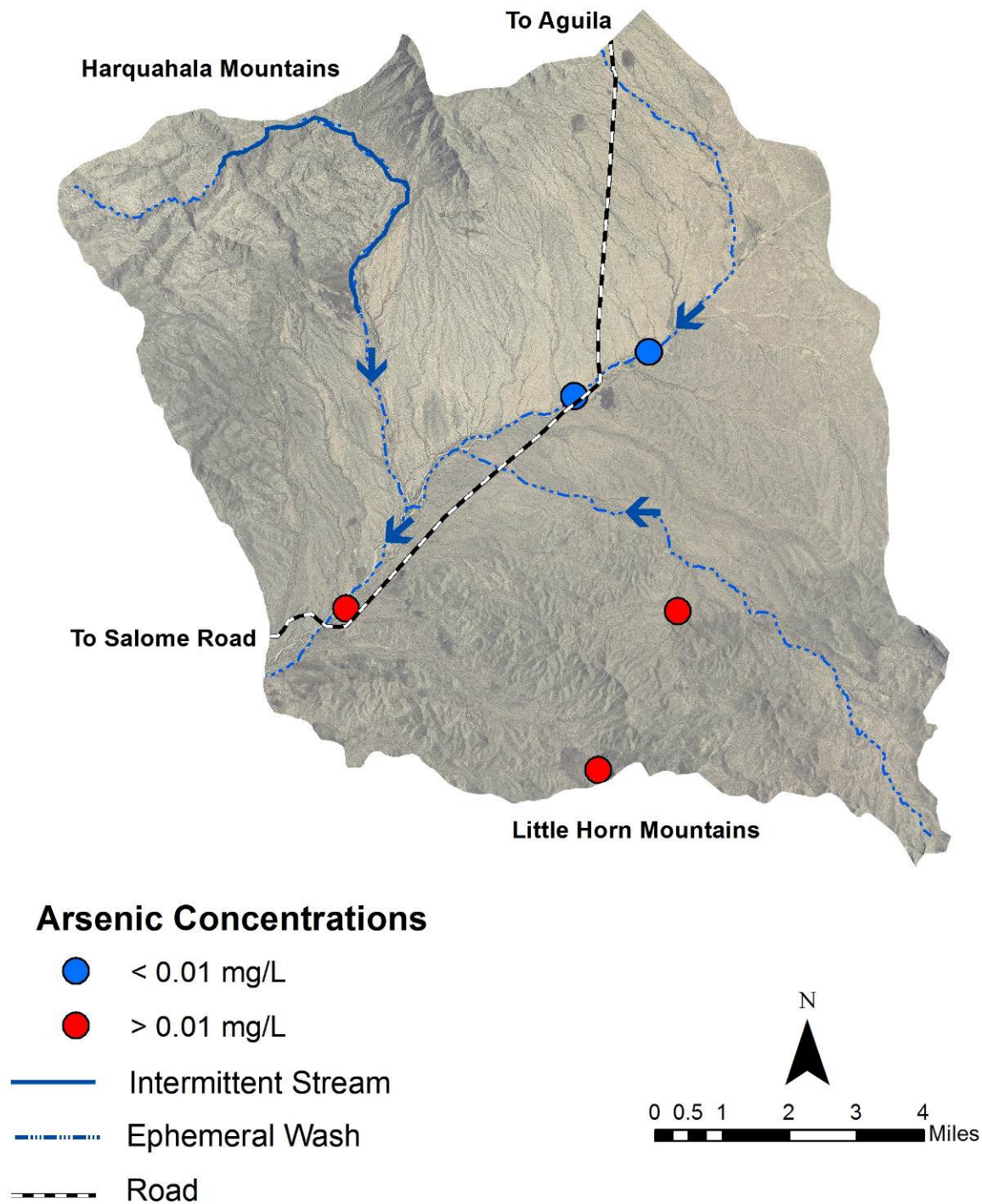
Map 5 - TDS



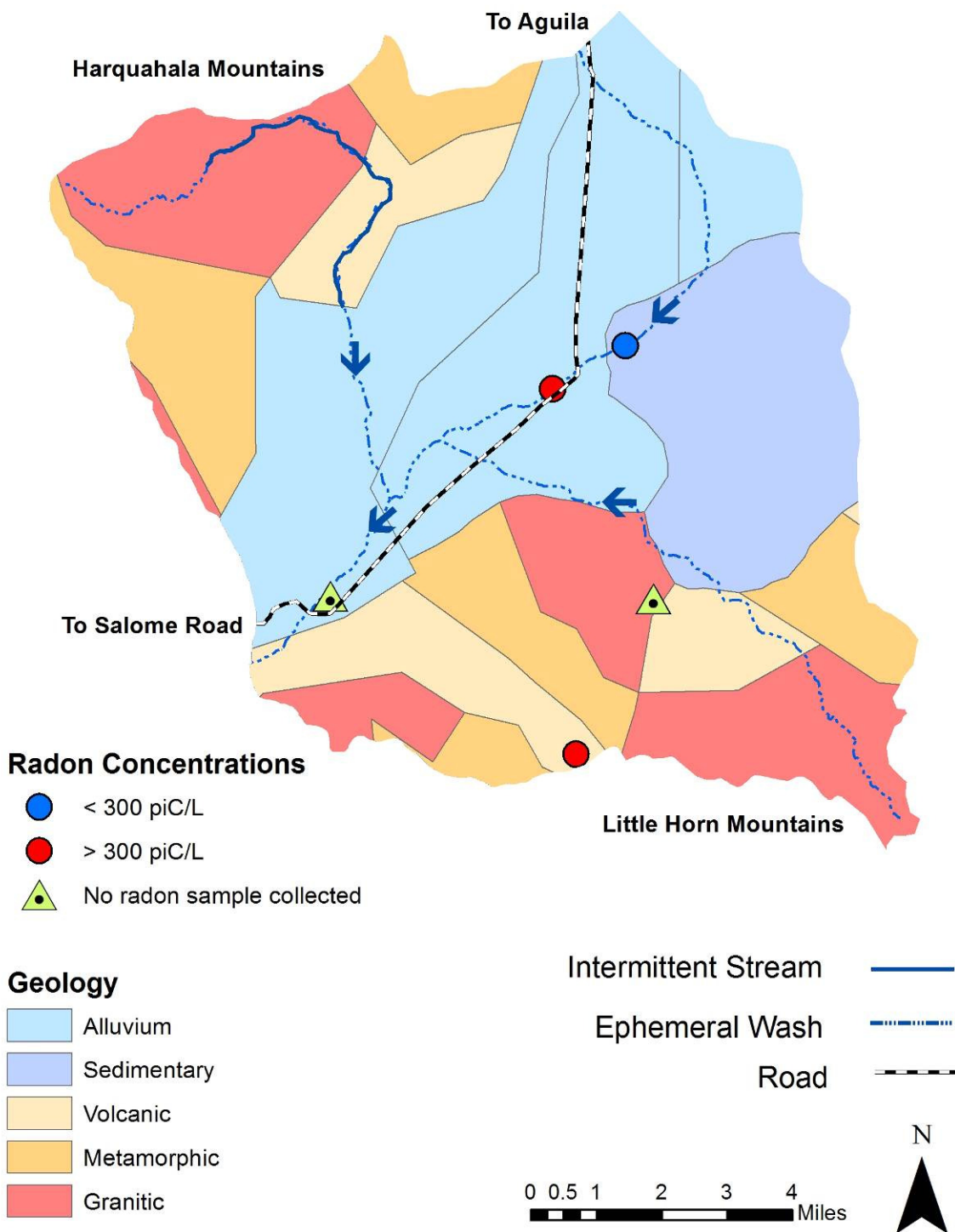
Map 6 - Nitrate



Map 7 - Arsenic



Map 8 - Radon and Geology



Isotopes

Oxygen and Hydrogen Isotopes - These samples were collected from five sites in the Tiger Wash basin and roughly conform to what would be expected in an arid environment, having a slope of 7.1, with the Local Meteoric Water Line (LMWL) described by the linear equation:

$$\delta D = 4.3 \delta^{18}O - 22.2$$

The LMWL for the Tiger Wash basin (Diagram 3) is similar to other basins in Arizona such as Aravaipa Canyon (4.1), Dripping Springs Wash (4.4), Upper Hassayampa and Harquahala (5.0), Detrital Valley (5.2), Agua Fria (5.3), Bill Williams (5.3), Sacramento Valley and Tonto Basin (5.5), Big Sandy (6.1), Butler Valley (6.4), Pinal Active Management Area (6.4), Gila Valley (6.4), San Simon (6.5), San Bernardino Valley (6.8), McMullen Valley (7.4), Lake Mohave (7.8), and Ranegras Plain (8.3).²³

Oxygen and deuterium isotopes values were characteristic of younger, enriched water that had experienced considerable evaporation. This conclusion is supported by their calcium-bicarbonate chemistry which is characteristic of recently recharged groundwater.¹⁹ Although younger, enriched isotope samples have been collected in limited areas in the Bill Williams, Butler Valley, McMullen Valley, and Ranegras Plain basins, most isotope samples collected in the western Arizona basins were lighter and more depleted than would be expected from recharge occurring at elevations in this region. This suggests that much of the groundwater was recharged long ago (8,000 to 12,000 years) during cooler climatic conditions.¹¹

Nitrogen Isotopes - Sources of nitrate in groundwater may be distinguished by measuring two stable isotopes of nitrogen, nitrogen-14 and nitrogen-15, often represented as $\delta^{15}N$. Although the percentage of the two isotopes is nearly constant in the atmosphere, certain chemical and physical processes preferentially utilize one isotope, causing a relative enrichment of the other isotope in the remaining reactants. Because of these isotopic fractionation processes, nitrate from various nitrogen sources has been shown to have different nitrogen isotope ratios. The $\delta^{15}N$ values have been cited as ranging from +2 to +9 per mil (‰) for natural soil organic matter, -3 to +3 for inorganic fertilizer, and +10 to +20 per mil for animal waste.^{20, 22}

Groundwater samples for $\delta^{15}N$ analysis were collected at five wells in the basin. The $\delta^{15}N$ values

Oxygen and Hydrogen Isotopes

Groundwater characterizations using oxygen and hydrogen isotope data may be made with respect to the climate and/or elevation where the water originated, residence within the aquifer, and whether or not the water was exposed to extensive evaporation prior to collection.⁹ This is accomplished by comparing oxygen-18 isotopes ($\delta^{18}O$) and deuterium (δD), an isotope of hydrogen, data to the Global Meteoric Water Line (GMWL). The GMWL is described by the linear equation:

$$\delta D = 8 \delta^{18}O + 10$$

where δD is deuterium in parts per thousand (per mil, ‰), 8 is the slope of the line, $\delta^{18}O$ is oxygen-18 ‰, and 10 is the y-intercept.⁹ The GMWL is the standard by which water samples are compared and is a universal reference standard based on worldwide precipitation without the effects of evaporation.

Isotopic data from a region may be plotted to create a Local Meteoric Water Line (LMWL) which is affected by varying climatic and geographic factors. When the LMWL is compared to the GMWL, inferences may be made about the origin or history of the local water.⁹ The LMWL created by $\delta^{18}O$ and δD values for samples collected at sites in the Tiger Wash basin plot mostly to the right of the GMWL.

Meteoric waters exposed to evaporation are enriched and characteristically plot increasingly below and to the right of the GMWL. Evaporation tends to preferentially contain a higher percentage of lighter isotopes in the vapor phase and causes the water that remains behind to be isotopically heavier. In contrast, meteoric waters that experience little evaporation are depleted and tend to plot increasing to the left of the GMWL and are isotopically lighter.⁹

Groundwater from arid environments is typically subject to evaporation, which enriches δD and $\delta^{18}O$, resulting in a lower slope value (usually between 3 and 6) as compared to the slope of 8 associated with the GMWL.⁹

ranged from +3.6 to +17.5 ‰ while nitrate values ranged at these sites ranged from 2.2 to 5.9 mg/L (Diagram 4).

Based on these isotope results, it appears that the nitrogen source is natural soil organic matter for three samples in which $\delta^{15}\text{N}$ values ranged from +3.6 to

+3.9 ‰.^{20, 22} In two samples with $\delta^{15}\text{N}$ values of 11.9 and 17.5 ‰, it appears that animal waste is the predominant contributor of nitrogen. The samples were collected respectively from Pump Mine Well and Tiger Well, both of which are frequently used by livestock for watering purposes.

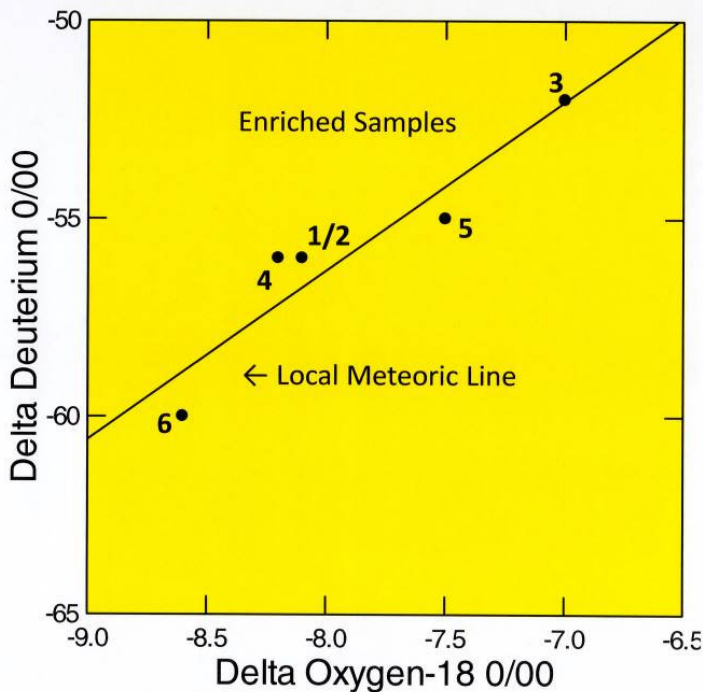


Diagram 3 – The five isotope samples are plotted according to their oxygen-18 and deuterium values and form the Local Meteoric Water Line. The samples all consist of enriched samples that contain younger water recharged from lower-elevation precipitation that has undergone the most evaporation prior to sampling. This is in contrast to most of the isotope samples collected in nearby western Arizona groundwater basins such as Butler Valley, Harquahala, and Ranegras Plain. Samples from these basins were mostly depleted and consisted of older recharge that had undergone less evaporation prior to sampling and appeared to reflect groundwater recharged during cooler climatic conditions.^{11, 23, 24, 25}

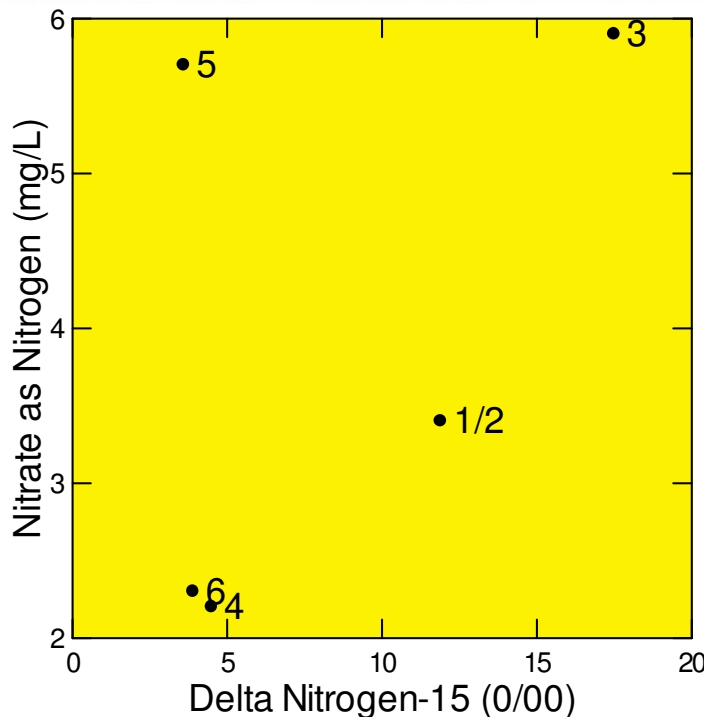


Diagram 4 – The five nitrogen isotope samples are plotted along with their corresponding nitrate (as N) concentrations. Samples from three sites (TIG-4, TIG-5, and TIG-6) appear to stem from natural soil organic matter while nitrogen from animal waste may impact the remaining two sites (TIG-1/2 and TIG-3).^{20, 22} However, these categories didn't appear to be accurate in the adjacent Harquahala basin where most $\delta^{15}\text{N}$ values corresponded with naturally occurring soil organic matter yet there was a strong statistical correlation between nitrate concentrations and areas of irrigated agriculture.²³

Time Trend Analysis

Site Comparison – Two wells sampled as part of the ADEQ study were previously sampled by the Arizona Department of Water Resources (ADWR) and/or the U.S. Geological Survey. Headquarters well (TIG-3) was part of the ADWR water quality index well network and was sampled in 1984, and every year between 1987 and 1996. Tiger well (TIG-4) was sampled both in 1980 and 1984. Time-trend comparisons between these samples are provided in Table 5, 6 and 7.

Substantial water quality changes took place at Old Headquarters well, with decreasing concentrations of many constituents. Particularly notable declines

include nitrate (46 percent), chloride (45 percent), and SC (19 percent) which all can be indicators of impacts from septic system impacts. The well owner has only operated the ranch for less than a decade but suggested that the Old Headquarters ranch house may have had considerable staff in the distant past but is now lightly used. Thus, the lesser inputs from septic systems may be now being reflected in the lower groundwater constituent concentrations of nitrate (Diagram 5), chloride (Diagram 6), and SC.³³

In contrast, Tiger well exhibited more consistent concentrations among constituents, with the exception of the fluoride result obtained in 1980.

Table 5. Summary of 30-Year (1984-2014) Time Trend Sample Results at Old Headquarters Well

Constituents	Difference in Percent	Difference in Concentration
Physical Parameters and General Mineral Characteristics		
Alkalinity, Total	+5 %	+18
SC-lab (µS/cm)	-19 %	-247
pH-field (su)	0 %	+0.04
pH-lab (su)	1 %	-0.1
Major Ions		
Calcium	-16 %	-13.6
Magnesium	-12 %	-4.4
Sodium	-15 %	-20.8
Potassium	-24 %	-1.3
Chloride	-45 %	-60.8
Sulfate	+20 %	+11.3
Nutrients		
Nitrate as N	-46 %	-10.1
Trace Elements		
Boron	+12 %	+0.041
Fluoride	+2 %	+0.01

All units are mg/L except as noted.

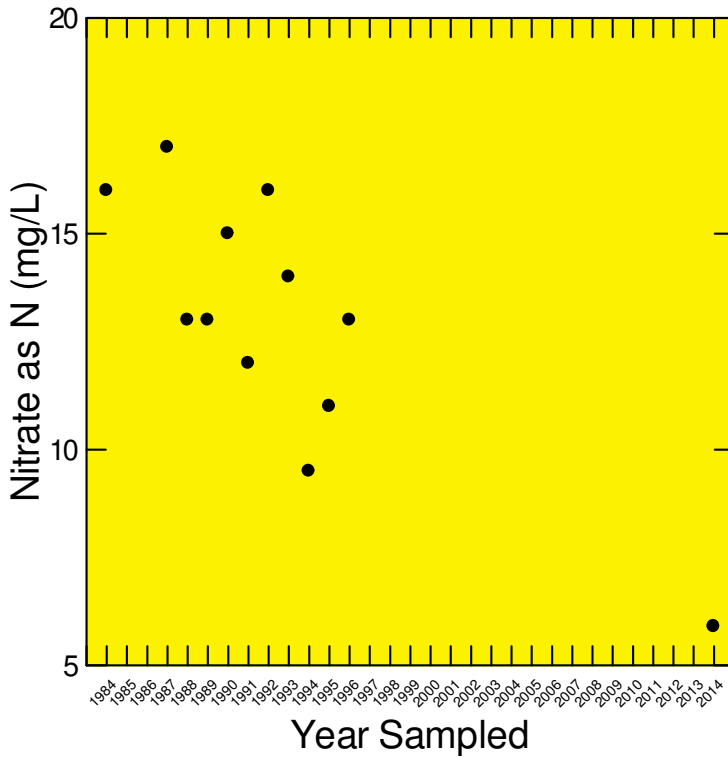


Diagram 5 – Old Headquarters well (TIG-3) was sampled 12 times over a 30-year period from 1984 to 2014. The nitrate (as N) concentrations have declined 46 percent during this time period, with the majority of the decrease occurring 18-year time period between 1996 and 2014.

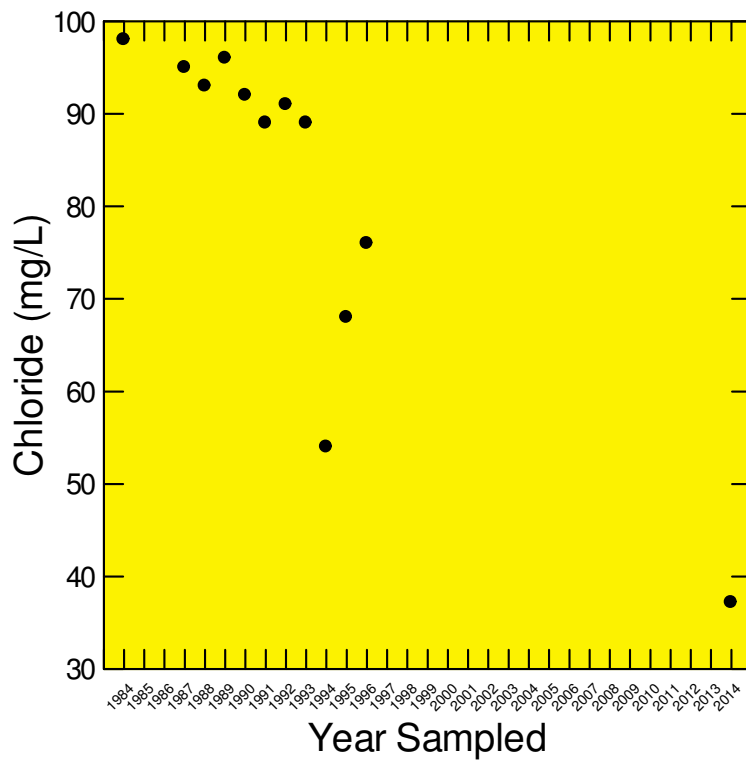


Diagram 6 – Old Headquarters well (TIG-3) was sampled 12 times over a 30-year period from 1984 to 2014. The chloride concentrations have declined 45 percent during this time period, with much of the decrease occurring after 1993.

Table 6. Summary of 34-Year (1980-2014) Time Trend Sample Results at Tiger Well

Constituents	Difference in Percent	Difference in Concentration
Physical Parameters and General Mineral Characteristics		
SC (µS/cm)	+8 %	+75
Trace Elements		
Fluoride	-72 %	-1.51

Table 7. Summary of 30-Year (1984-2014) Time Trend Sample Results at Tiger Well

Constituents	Difference in Percent	Difference in Concentration
Physical Parameters and General Mineral Characteristics		
Alkalinity, Total	+1 %	+6
SC-lab (µS/cm)	0 %	0
pH-field (su)	+1 %	+0.12
pH-lab (su)	-2 %	-0.25
Major Ions		
Calcium	-3 %	-3.6
Magnesium	+9 %	+3.0
Sodium	+11 %	+4.1
Potassium	-6 %	-0.35
Chloride	+15 %	+2.2
Sulfate	-5 %	-0.9
Nutrients		
Nitrate as N	+33 %	+1.1
Trace Elements		
Arsenic	+10 %	+0.0022
Barium	-23 %	-0.0195
Fluoride	-2 %	-0.01
Strontium	+12 %	+0.161
Zinc	+89 %	+0.578

All units are mg/L except as noted.

DISCUSSION

Groundwater in the Tiger Wash basin is generally of good quality with the exception of arsenic concentrations. Of the five sites sampled, three had arsenic concentrations that exceeded federal health-based, Primary MCLs and one site exceeded the state arsenic standard. Otherwise, all health and aesthetic drinking water quality standards were met at all five sites. Arsenic is the constituent that most commonly exceeds health-based water quality standards in Arizona.²⁷ This trace element is likely naturally occurring in the basin.

Arsenic concentrations are affected by reactions with hydroxyl ions and are influenced by factors such as an oxidizing environment, lithology, and aquifer residence time.¹⁹ Oxygen and hydrogen isotope values suggest that groundwater in the basin is younger, enriched water that has experienced considerable evaporation, so aquifer residence time does not appear to be a major factor.¹¹

Nearby basins Bill Williams, Butler Valley, Harquahala, and Ranegras Plain have limited groundwater sites that consist of younger, enriched water. For the most part, enriched samples from these sites do not have elevated concentrations of arsenic.^{23, 24, 25, 26} This suggests that local lithology at the three Tiger Wash sites which include granitic, volcanic, and alluvial geology are a major factor in creating elevated arsenic concentrations.

Limited time trend analysis involving two wells had inconclusive results. Historic sampling results from Tiger well (TIG-4) suggested generally steady constituent concentrations including arsenic levels which exceed the Primary MCL. Previous sample results from Headquarters well (TIG-3), however, indicated that concentrations of many constituents decreased, some dramatically. Emblematic are nitrate concentrations which were measured at 13 mg/L in 1996 and declined below the Primary MCL to 5.9 mg/L by 2014. Possible explanations for decreasing constituent concentrations at Headquarters well include less input from the onsite septic system.³³

REFERENCES

- ¹ Accutest, 2014. Personal communication from Test America staff.
- ² Arizona Department of Environmental Quality, 1991. *Quality Assurance Project Plan: Arizona Department of Environmental Quality Standards Unit*, 209 p.
- ³ Arizona Department of Environmental Quality, 2013-2014. *Arizona Laws Relating to Environmental Quality*: St. Paul, Minnesota, West Group Publishing, §49-221-224, p 134-137.
- ⁴ Arizona State Land Department, 1997. "Land Ownership - Arizona" GIS coverage: Arizona Land Resource Information Systems, downloaded, 9/10/14.
- ⁵ Arizona Department of Water Resources website, 2014. www.azwater.gov/azdwr/default.aspx, accessed 08/12/14.
- ⁶ Arizona Water Resources Research Center, 1995. *Field Manual for Water-Quality Sampling*: Tucson, University of Arizona College of Agriculture, 51 p.
- ⁷ Bitton, G. and Gerba, C.P., 1994. *Groundwater Pollution Microbiology*: Malabar, FL: Krieger Publishing Company, 377 p.
- ⁸ Cook, D., 2009. "Toxic mine tailings no longer headed for Iron King Mine," *Prescott Daily Courier*: Prescott, AZ, August 25, www.dcourier.com/main.asp?SectionID=1&subsectionID=1&articleID=71736
- ⁹ Craig, H., 1961. Isotopic variations in meteoric waters. *Science*, 133, pp. 1702-1703.
- ¹⁰ Crockett, J.K., 1995. Idaho statewide groundwater quality monitoring program—Summary of results, 1991 through 1993: Idaho Department of Water Resources, Water Information Bulletin No. 50, Part 2, p. 60.
- ¹¹ Earman, Sam, et al, 2003. An investigation of the properties of the San Bernardino groundwater basin, Arizona and Sonora, Mexico: Hydrology program, New Mexico Institute of Mining and Technology, 283 p.
- ¹² Graf, Charles, 1990. An overview of groundwater contamination in Arizona: Problems and principals: Arizona Department of Environmental Quality seminar, 21 p.
- ¹³ Heath, R.C., 1989. Basic ground-water hydrology: U.S. Geological Survey Water-Supply Paper 2220, 84 p.

- ¹⁴ Hedley, J.D., 1990. Maps showing ground-water conditions in the Harquahala Irrigation Non-Expansion area and Tiger Wash basin, Maricopa and La Paz Counties, Arizona—1989; Arizona Department of Water Resources Hydrologic Map Series Report Number 17, 3 sheets, scale, 1:250,000.
- ¹⁵ Hem, J.D., 1985. Study and interpretation of the chemical characteristics of natural water [Third edition]: U.S. Geological Survey Water-Supply Paper 2254, 264 p.
- ¹⁶ Lowry, J.D. and Lowry, S.B., 1988. "Radionuclides in Drinking Waters," in *American Water Works Association Journal*, 80 (July), pp. 50-64.
- ¹⁷ Madison, R.J., and Brunett, J.O., 1984. Overview of the occurrence of nitrate in ground water of the United States, in *National Water Summary 1984-Water Quality Issues*: U.S. Geological Survey Water Supply Paper 2275, pp. 93-105.
- ¹⁸ Richard, S.M., Reynolds, S.J., Spencer, J.E. and Pearthree, P.A., 2000. Geologic map of Arizona: Arizona Geological Survey Map 35, scale 1:1,000,000.
- ¹⁹ Robertson, F.N., 1991. Geochemistry of ground water in alluvial basins of Arizona and adjacent parts of Nevada, New Mexico, and California: U.S. Geological Survey Professional Paper 1406-C, 90 p.
- ²⁰ Sustainability of Semi-Arid Hydrology and Riparian Areas website, <http://web.sahra.arizona.edu/programs/isotopes/nitrogen.html#2>, accessed 9/10/14.
- ²¹ Test America, 2014. Personal communication from Test America staff.
- ²² Thiros, S.A., Bexfield, L.M., Anning, D.W., and Huntington, J.M., eds., 2010. Conceptual understanding and groundwater quality of selected basin-fill aquifers in the Southwestern United States: U.S. Geological Professional Paper 1781, 288 p.
- ²³ Towne, D.C., 2014. Ambient groundwater quality of the Harquahala basin: a 2009-2014 baseline study: Arizona Department of Environmental Quality Open File Report 14-04, 62 p.
- ²⁴ Towne, D.C., 2012. Ambient groundwater quality of the Butler Valley basin: a 2008-2012 baseline study: Arizona Department of Environmental Quality Open File Report 12-06, 44 p.
- ²⁵ Towne, D.C., 2011. Ambient groundwater quality of the Ranegras Plain basin: a 2008-2011 baseline study: Arizona Department of Environmental Quality Open File Report 11-07, 63 p.
- ²⁶ Towne, D.C., 2011. Ambient groundwater quality of the Ranegras Plain basin: a 2008-2011 baseline study: Arizona Department of Environmental Quality Open File Report 11-07, 63 p.
- ²⁷ Towne, Douglas and Jones, Jason, 2011. Groundwater quality in Arizona: a 15 year overview of the ADEQ ambient groundwater monitoring program (1995-2009): Arizona Department of Environmental Quality Open File Report 11-04, 22 p.
- ²⁸ University of Arizona Environmental Isotope Laboratory, 2014. Personal communication from Christopher Eastoe.
- ²⁹ U.S. Environmental Protection Agency website, www.epa.gov/waterscience/criteria/humanhealth/, accessed 9/10/14.
- ³⁰ U.S. Environmental Protection Agency website, <http://water.epa.gov/lawsregs/rulesregs/sdwa/radon/regulations.cfm>, accessed 9/10/14.
- ³¹ U.S. Salinity Laboratory, 1954. Diagnosis and improvement of saline and alkali soils: U.S. Department of Agriculture, Agricultural Research Service, Agriculture Handbook No. 60, 160 p.
- ³² Wilkinson, L., and Hill, M.A., 1996. *Using Systat 6.0 for Windows*, Systat: Evanston, Illinois, p. 71-275.
- ³³ Overson, Clayton, 2014. Personal communication from ranch owner, 10/8/14.

Appendix A. Data for Sample Sites, Tiger Wash Basin, 2014

Site #	Cadastral / Pump Type	Latitude - Longitude	ADWR #	ADEQ #	Site Name	Samples Collected	Well Depth	Water Depth	Year Drilled
1 st Field Trip, January 17, 2014 – Towne									
TIG-1/2 split	B(5-9)03cca submersible	33°48'02.034" 113°11'25.783"	612680	18403	Pump Mine Well	Inorganic, Radiochem Radon, O,H, N isotope	-	-	
TIG-3	B(5-9)02bdd windmill	33°48'30.197" 113°10'27.792"	612682	18402	HQ Windmill	Inorganic, Radon O,H & N Isotopes	400'	200'	
TIG-4	B(5-9)19bdd windmill	33°45'44.927" 113°14'22.620"	612691	18398	Tiger Windmill	Inorganic O,H & N Isotopes	235'	90'	
2 nd Field Trip, February 10 & 11, 2014 – Towne & Boettcher & Dickens									
TIG-5	B(5-9)34acb windmill	33°44'00.870" 113°11'07.114"	612689	18401	Little Horn Windmill	Inorganic, Radiochem Radon, O,H, N isotope	360'	250'	
TIG-6	B(5-9)23bdd windmill	33°45'43.224" 113°10'05.423"	612690	18399	Pegrin Windmill	Inorganic O,H & N Isotopes	520'	180'	

Appendix B. Groundwater Quality Data, Tiger Wash Basin, 2014

Site #	MCL Exceedances	Temp (°C)	pH-field (su)	pH-lab (su)	SC-field (µS/cm)	SC-lab (µS/cm)	TDS-field (mg/L)	TDS-lab (mg/L)	Hard (mg/L)	Turb (ntu)
TIG-1/2		22.3	7.58	7.58	420	441	273	279.5	222	2.75
TIG-3		20.9	7.74	7.70	528	538	341	304	153	8.9
TIG-4	As	19.3	7.32	7.15	472	495	307	286	224	ND
TIG-5	As	24.8	7.64	7.88	526	540	318	333	240	ND
TIG-6	As	24.5	7.92	8.19	345	284	224	215	126	ND

italics = constituent exceeded holding time

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Tiger Wash Basin, 2014--Continued

Site #	Calcium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Potassium (mg/L)	T. Alk (mg/L)	Bicarbonate (mg/L)	Carbonate Alk (mg/L)	Hydroxide Alk (mg/L)	Chloride (mg/L)	Sulfate (mg/L)
TIG-1/2	53.5	20.6	17.25	2.12	229	279	ND	ND	5.45	6.5
TIG-3	35.4	15.6	57.2	2.17	174	212	ND	ND	37.2	34.3
TIG-4	58.4	19.0	20.1	2.75	250	305	ND	ND	8.7	8.3
TIG-5	43.8	31.7	33.2	1.88	228	278	ND	ND	20	12.1
TIG-6	18.9	19.1	23.1	1.01	192	234	ND	ND	7.8	4.5

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Tiger Wash Basin, 2014--Continued

Site #	Nitrate-N (mg/L)	$\delta^{15}\text{N}$ (‰)	Nitrite-N (mg/L)	TKN (mg/L)	Ammonia (mg/L)	T. Phos. (mg/L)	SAR (value)	Irrigation Quality	Alum (mg/L)	Strontium (mg/L)
TIG-1/2	3.4	11.9	ND	4.4/nd	ND/.092	ND/.010	0.5	C2-S1	ND	0.6725
TIG-3	5.9	17.5	ND	0.29	ND	ND	2.0	C2-S1	ND	0.571
TIG-4	2.2	4.5	ND	0.50	ND	0.022	0.6	C2-S1	ND	0.761
TIG-5	5.7	3.6	ND	ND	ND	0.035	0.9	C2-S1	ND	1.29
TIG-6	2.3	3.9	ND	ND	ND	0.033	0.9	C2-S1	ND	0.684

italics = constituent exceeded holding time

Appendix B. Groundwater Quality Data, Tiger Wash Basin, 2014--Continued

Site #	Antimony (mg/L)	Arsenic (mg/L)	Barium (mg/L)	Beryllium (mg/L)	Boron (mg/L)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Fluoride (mg/L)
TIG-1/2	ND	0.00395	0.0558	ND/.00026	ND/.06 1	ND	ND/.00092	ND/.002 4	0.097
TIG-3	ND	ND	0.0748	ND	0.191	ND	ND	0.0076	0.21
TIG-4	ND	0.0122	0.0335	ND	ND	ND	ND	0.0154	0.29
TIG-5	ND	0.0261	0.0022	ND	ND	ND	0.0396	0.0042	0.43
TIG-6	ND	0.0602	ND	ND	0.138	ND	0.0034	ND	0.94

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level

Appendix B. Groundwater Quality Data, Tiger Wash Basin, 2014--Continued

Site #	Iron (mg/L)	Lead (mg/L)	Manganese (mg/L)	Mercury (mg/L)	Nickel (mg/L)	Selenium (mg/L)	Silver (mg/L)	Thallium (mg/L)	Zinc (mg/L)
TIG-1/2	ND	ND/.000 40	ND/.00064	ND	ND	ND	ND	ND	0.231
TIG-3	ND	ND	0.0268	ND	ND	ND	ND	ND	0.316
TIG-4	ND	ND	ND	ND	ND	ND	ND	ND	0.614
TIG-5	ND	ND	ND	ND	ND	ND	ND	ND	0.233
TIG-6	ND	ND	ND	ND	ND	ND	ND	ND	0.827

Appendix B. Groundwater Quality Data, Tiger Wash Basin, 2014--Continued

Site #	Radon-222 (pCi/L)	Alpha (pCi/L)	Beta (pCi/L)	Ra-226 + Ra-228 (pCi/L)	Uranium (µg/L)	* ¹⁸ O (‰)	* D (‰)	Type of Chemistry
TIG-1/2	319	5.9	-	-	4.0	-8.1	-56	calcium-bicarbonate
TIG-3	152	-	-	-	-	-7.0	-52	mixed-bicarbonate
TIG-4	-	-	-	-	-	-8.2	-56	calcium-bicarbonate
TIG-5	524	1.8	-	-	1.5	- 7.5	- 55	magnesium-bicarbonate
TIG-6	-	-	-	-	-	- 8.6	- 60	magnesium-bicarbonate

bold = constituent concentration exceeded Primary or Secondary Maximum Contaminant Level